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Manganese in water supplies.

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MANGANESE IN WATER SUPPLIES

BY

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B. S. New Hampshire College, 1910

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INTRODUCTION

Water supplies containing manganese have been considered uncommon in the United States. In but few laboratories are manganese determinations made as a part of the general routine work of water analysis. Even in the selection of a water supply for a community, the question of manganese content is seldom considered.

In April, 1911, the attention of the Illinois State Water Survey was called to a serious incrustation which had formed in the city water system of Mt. Vernon, Illinois.* An analysis showed that this incrustation con-

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*University of Illinois Bulletin, Water Survey Series No. 10, pp. 57-65. (1913)

---

tained from 4.4 to 8.8 percent. of manganese and that the original water contained 0.6 parts per million of this element. Later, manganese was found in a number of other water supplies of the state, both public and private.

Manganese in a water supply is objectionable for the following reasons. It deposits in the water pipes causing a dark incrustation. In some instances this de-

posit is so extensive as to cause complete stoppage. It stains plumbing fixtures a dark color due to the separation of the dioxide. It also stains fabrics yellow or brown when used in the laundry. In these respects manganese bearing waters resemble waters which contain iron, but the deposits are darker and more difficult to remove than those produced by waters which contain iron.

On account of the economic importance of this subject, the present investigation was undertaken. The problem has been studied from the standpoints of: (I) the analytical determination of the element, (II) its occurrence and distribution, and (III) its removal from water supplies.

PART I.

THE DETERMINATION OF MANGANESE IN WATER SUPPLIES

Theoretically, it might seem that any accurate method for the determination of manganese in substances could be successfully applied to the determination of the element in water. In practice, however, many of these methods are wholly impractical. Manganese occurs in water in relatively small amounts, usually only a small fraction of a milligram per liter. In some cases several milligrams per liter are found, but instances in which more than ten parts per million of the element are encountered are very uncommon. Other salts are present in natural waters in many times as large amounts as are the manganous salts. These conditions eliminate some of the accurate and standard methods for the determination of manganese.

For these reasons, the gravimetric and the volumetric methods in general use are not applicable. If they are used, under most conditions, large volumes of water must be evaporated in order to procure a sufficient quantity of the element for determination. Possibly, in making the complete analysis of the mineral content of water samples, this procedure would not be seriously objectionable, but for rapid work, such as the analytical

control of a manganese removal plant, it would be wholly impractical.

To be sure, several water analysts have recommended volumetric or gravimetric methods for manganese.

Lührig and Becker* report satisfactory results

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*Pharm. Zentralhalle, 48, 137-42. (1907)

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in applying Knorre's* persulfate peroxide method to the

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*Z. angew. Chem. 14, 1149-62. (1901)

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determination of manganese in water. If the water contains less than ten milligrams of Mn per liter, however, they state that it must be concentrated by evaporation. H. Klut* also recommends the same method for use in those

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*Mitt. kgl. Prüfungsanst. Wasserversorg. Abwasserbeseit., 1909, 12, 182-94.

---

cases where the manganese content is over ten milligrams per liter. He states, however, that from five to ten liters of the sample should be used.

J. Prescher* recommends that the manganese be

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*Pharm. Zentralhalle 47, 799-802. (1906)

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ammonium persulfate, $(NH_4)_2S_2O_8$.

The 1912 edition of "Standard Methods of Water Analysis" published by the American Public Health Association gives the bismuthate and the lead peroxide methods for the determination of amounts of manganese of less than ten milligrams per liter. If more than this amount is present, Knorre's* volumetric persulfate method is

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*Z. angew. Chem. 14, 1149-62. (1901)

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recommended. These are presumed to be the official methods to be used by water analysts in making manganese determinations. In the Bureau of Chemistry, U. S. Department of Agriculture*, the colorimetric persulfate method is used.

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*Bull. 152, U.S. Dept. of Agr.,
Bureau of Chemistry, 78. (1912)

Upon inquiry, it was found that no water chemists used the lead peroxide method. Owing to the fact that there are several methods in use for determining manganese in water, and that some literature has accumulated concerning their accuracy and the sources of error, it seemed advisable to make a careful comparison of them for the proposed revision of "Standard Methods of Water Analysis".

Accordingly, the three colorimetric methods

were carefully compared,

1. The Lead Peroxide Method.
2. The Sodium Bismuthate Method.
3. The Ammonium Persulfate Method.

PREPARATION OF SOLUTIONS

Several solutions of known manganese content were first carefully prepared.

Solution 1, Manganous Chloride.

For the preparation of water samples of known manganese content, a standard manganous chloride solution was prepared by dissolving approximately 32 grams of pure manganous chloride, $MnCl_2 \cdot 4H_2O$, in a liter of distilled water. The manganese chloride was purified as follows. About 200 grams of Baker's Analyzed manganous chloride were dissolved in a liter of distilled water. This solution was boiled with a small amount of manganese carbonate prepared by adding sodium carbonate to a portion of the original solution, then filtering, and washing the precipitate. Possible traces of iron, aluminum and chromium were thus removed. The whole was then filtered after which the filtrate was treated with ammonium sulfide to remove copper, lead, etc. The solution was then acidified with hydrochloric acid and boiled to remove hydrogen sulfide, after which it was filtered. A small amount of copper

which was present was thus removed. Sodium carbonate was next added in excess. The manganous carbonate was filtered and washed free from chlorides. Most of this precipitate was then dissolved in hydrochloric acid. A small portion of that which was undissolved was added to the solution, and the whole was boiled and filtered. Upon evaporation, crystalline manganous chloride was obtained. The chloride in the standard solution was determined gravimetrically, and the amount of manganese was calculated. Manganese was also directly determined by evaporating a 50 cc. portion of the solution with sulfuric acid, heating and weighing as $MnSO_4$. Gooch and Austin*

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*Z. anorg. Chem. 17, 264-71. (1898)

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have shown that this method is accurate. The average of triplicate determinations by each method gave the following results:

By determining chlorine as AgCl.

1 cc. = 1.604 milligrams of chlorine.

1 cc. = 1.245 " " manganese.

By determining manganese as $MnSO_4$.

1 cc. = 1.254 milligrams of manganese.

The mean of these two values was taken as the strength of the solution, or,

1 cc. = 1.250 milligrams of manganese.

This solution was then diluted to one-tenth of its strength, so that

1 cc. = 0.125 milligrams of manganese.

Solution 2, Potassium Permanganate.

For the preparation of permanganate standards by simple dilution, a standard solution was prepared from Kahlbaum's potassium permanganate, after crystallizing twice from double distilled water and drying over sulfuric acid. In one liter of water 0.2880 grams of the salt were dissolved. The strength of this solution was, therefore, assumed to be:

1 cc. = 0.100 milligrams of manganese.

Solution 3, Manganous Sulfate.

Dilute solutions of permanganate are not very stable.* In order to check their value and to have

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*Morse, Hopkins and Walker,
Am. Chem. J. 18, 401-19. (1896)

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standards prepared in exactly the same manner the sample was treated. 0.2280 grams of potassium permanganate were dissolved in water, and reduced to manganous sulfate by heating with sulfuric acid and a slight excess of oxalic acid, after which the whole was diluted to one liter. This manganous sulfate solution was of such strength that,

1 cc. = 0.100 milligram of manganese.

THE LEAD PEROXIDE METHOD

The lead peroxide method, first brought out by Crum*, has been used for a long time in iron and steel

*Ann. 55, 219. (1845)

work. It has, however, been used to only a limited extent in water work. At present, it has been largely supplanted by the bismuthate and persulfate methods. Of some twelve investigators who have worked on the determination of manganese in water during the past ten years, only one, H. Klutt*, recommends this method. The

*Mitt. kgl. Prüfungsanst. Wasserversorg. Abwasserbeseit., 1909, 12, 182-94.

majority favor the persulfate method, while the bismuthate method seems to be second in popularity. No one, however, appears to have carefully compared the three methods. The material embodied in the section dealing with manganese in "Standard Methods of Water Analysis", 1912, appears to have been based entirely upon the work of Klutt* and of R. S. Weston**.

*Loc. cit.
**J. Am. Chem. Soc. 29, 1074-8. (1907)

The first experimental work with the lead peroxide method was carried out according to the following procedure.

Varying amounts of the standard manganous chloride solution were diluted with distilled water, and evaporated in beakers with two or three drops of sulfuric acid until white fumes appeared. They were then diluted with water and acidified with 10 cc. of dilute nitric acid free from brown oxides of nitrogen, and boiled down to a volume of 50 cc. 0.5 gram of lead peroxide was added, and the solution was boiled for five minutes. It was then filtered thru a Gooch crucible, previously prepared with asbestos, ignited, treated with permanganate, and washed with water. The filtrate was transferred to a Nessler tube and the color was compared immediately with standards made by diluting a standard solution of potassium permanganate (1cc. = 0.1 mg. Mn) with water acidified with sulfuric acid.

The results obtained by this method are shown in Table I. They indicate that the amounts of manganese found were in nearly all cases lower than the amounts actually present. The mean difference in the twenty-five determinations made was .027 milligrams.

In order to check the possibility of error due to the manganous chloride and the potassium permanganate solutions not being of the same manganese content another

TABLE I.

DETERMINATION OF MANGANESE BY THE LEAD PEROXIDE METHOD I.

Known $MnCl_2$ Solutions in Distilled Water Compared with Diluted $KMnO_4$ Standards.

cc. $MnCl_2$	cc. $KMnO_4$ (Standard)	Milligrams of Manganese Found	Theory	Difference
0.0	0.0	.00	.00	- .00
0.2	0.0	.00	.025	- .025
0.2	0.0	.00	.025	- .025
0.4	0.2	.02	.050	- .03
0.4	0.2	.02	.050	- .03
0.6	0.3	.03	.075	- .045
0.6	0.4	.04	.075	- .035
0.8	0.7	.07	.100	- .03
0.8	0.6	.06	.100	- .04
1.0	1.0	.10	.125	- .025
1.0	1.0	.10	.125	- .025
1.2	1.2	.12	.150	- .03
1.2	1.3	.13	.150	- .02
1.5	1.8	.18	.187	- .007
1.5	1.8	.18	.187	- .007
2.0	2.5	.25	.250	.00
2.0	2.3	.23	.250	- .02
2.5	2.8	.28	.312	- .032
2.5	2.5	.25	.312	- .062
3.0	3.5	.35	.375	- .025
3.0	3.5	.35	.375	- .025
3.5	4.0	.40	.438	- .038
3.5	4.0	.40	.438	- .038
4.0	4.5	.45	.500	- .050
4.0	5.0	.50	.500	.000
			Mean . . .	- .027

series of determinations was made using diluted portions of the potassium permanganate solution instead of the manganous chloride solution. These portions were treated as previously described and were then compared with standards prepared from the same potassium permanganate solution. The results of this series of tests are shown in Table II.

The average amount found was .027 milligrams less than that actually present, altho the differences were variable. When small amounts, .00 to .10 milligram, are present, the error is as great as 50 percent. The error becomes reduced to about 10 percent., however, when the amount present increases to .3 or .4 milligrams. It is, however, a serious error.

These figures indicate that as this determination is carried out, either the oxidation to permanganate is not complete or there is some reduction in subsequent steps,. as the color produced is not so deep as that produced by a standard potassium permanganate solution diluted to the same manganese content.

A series of determinations was made, therefore, in which the standards used for comparison were made from the manganous sulfate solution treated in the same manner as the samples were treated, on the supposition that standards thus prepared should be exactly comparable with the sample. The results obtained are shown in Table III.

TABLE II.

DETERMINATION OF MANGANESE BY THE LEAD PEROXIDE METHOD II.

Known $KMnO_4$ Solutions in Distilled Water Compared with Diluted $KMnO_4$ Standards.

cc. $KMnO_4$	cc. $KMnO_4$ (Standard)	Milligrams of Manganese Found	Theory	Difference
0.0	0.0	.00	.00	.00
0.2	0.0	.00	.02	- .02
0.2	0.0	.00	.02	- .02
0.4	0.15	.015	.04	- .025
0.4	0.10	.01	.04	- .03
0.6	0.3	.03	.06	- .03
0.6	0.3	.03	.06	- .03
0.8	0.4	.04	.08	- .04
0.8	0.5	.05	.08	- .03
1.0	0.8	.08	.10	- .02
1.0	0.8	.08	.10	- .02
1.2	1.0	.10	.12	- .02
1.2	0.9	.09	.12	- .03
1.5	1.2	.12	.15	- .03
1.5	1.2	.12	.15	- .03
2.0	1.8	.18	.20	- .02
2.0	2.0	.20	.20	.00
2.5	2.2	.22	.25	- .03
2.5	2.2	.23	.25	- .02
3.0	2.2	.22	.30	- .07
3.0	2.5	.25	.30	- .05
3.5	3.0	.30	.35	- .05
3.5	3.2	.32	.35	- .03
4.0	4.0	.40	.40	.00
4.0	3.7	.37	.40	- .03
			Mean	- .027

TABLE III.

DETERMINATION OF MANGANESE BY THE LEAD PEROXIDE METHOD III.

Known $MnCl_2$ Solutions in Distilled Water Compared with $MnSO_4$ Standards. Treated in the Same Manner.

cc. $MnCl_2$	cc. $MnSO_4$ (Standard)	Milligrams of Manganese Found	Theory	Difference
0.0	0.0	.00	.00	.00
0.2	0.0	.00	.025	- .025
0.2	0.0	.00	.025	- .025
0.4	0.6	.06	.050	+ .01
0.4	0.4	.04	.050	- .01
0.6	0.8	.08	.075	+ .005
0.6	0.4	.04	.075	- .035
0.8	1.2	.12	.100	+ .02
0.8	1.5	.15	.100	+ .05
1.0	1.1	.11	.125	- .015
1.0	1.2	.12	.125	- .005
1.2	1.0	.10	.150	- .05
1.2	1.1	.16	.150	+ .01
1.5	2.3	.23	.187	+ .043
1.5	2.0	.20	.187	+ .013
2.0	1.8	.18	.250	- .07
2.0	1.9	.28	.250	+ .03
2.5	3.0	.30	.312	- .012
2.5	3.2	.32	.312	+ .008
3.0	4.0	.40	.375	+ .025
3.0	4.0	.40	.375	+ .025
3.5	3.5	.35	.438	- .088
3.5	4.0	.40	.438	- .038
4.0	5.0	.50	.500	- .000
4.0	6.0	.60	.500	+ .100
			Mean . . .	- .020

The results obtained were very erratic, some being too high and some too low. Even when carried out under conditions which were as nearly as possible the same, it was impossible to obtain checks. In many cases the error was as high as 30 percent.

It was thot that the most probable source of error in the determination was in filtering thru asbestos. A very small amount of reducing agent would easily affect such very dilute permanganate solutions. A small amount of organic matter or the presence of manganese compounds in the filter medium might have caused the reductions.

In order to eliminate this factor, the determinations were made without filtration. One series was carried thru with samples prepared from distilled water, using manganous chloride. The subsequent comparisons were made, after decanting into Nessler tubes, with manganous sulfate standards treated in all respects like the samples. A second series was like the first except that the comparison of the solutions was made in the original beakers after allowing the lead peroxide to settle. A third was like the second except that the original samples were prepared by adding the manganous chloride solution to tap water instead of distilled water. The tap water is a bicarbonate water from deep wells. It contains practically no chlorides or sulfates. It has a turbidity of 5 parts per million and a color of 15 parts per million, due

to its content of iron and organic matter. The iron content is two parts per million. The water is free from manganese. The results obtained in these three series of determinations are shown in Tables IV, V and VI.

These results show a much greater accuracy than when the solutions were filtered thru asbestos.

In the series in which the color comparisons were made after decanting the supernatant liquid to Nessler tubes, difficulty was experienced on account of incomplete settling of the lead peroxide. Some was invariably carried over causing a dark color which rendered the color comparisons difficult. In the series in which color comparisons were made in the original beakers, this difficulty was not encountered. The colors cannot be matched so accurately in beakers, however, as the relatively thin layers make the differences in color appear less marked. The determinations made with tap water are as accurate as those with distilled water.

Manganese can, therefore, be determined with a fair degree of accuracy by this method in waters which contain little chlorine and organic matter. .02 milligrams can be detected in a volume of 50 cc. by color comparison in Nessler tubes.

Organic matter in large amounts unless removed causes error, altho in ordinary samples the error is inappreciable as the results with tap water show.

TABLE IV.

DETERMINATION OF MANGANESE BY THE LEAD PEROXIDE METHOD IV.

Known $MnCl_2$ Solutions in Distilled Water Compared with $MnSO_4$ Standards. Treated in Same Manner and Decanted to Nessler Tubes.

cc. $MnCl_2$	cc. $MnSO_4$ (Standard)	Milligrams of Manganese Found	Theory	Difference
0.0	0.0	.00	.00	.00
0.2	0.2	.02	.025	- .005
0.2	0.2	.02	.025	- .005
0.4	0.5	.05	.050	.00
0.4	0.6	.06	.050	+ .01
0.6	0.7	.07	.075	- .005
0.6	0.8	.08	.075	+ .005
0.8	1.2	.12	.100	+ .02
0.8	1.0	.10	.100	.00
1.0	1.2	.12	.125	- .005
1.0	1.0	.10	.125	- .025
1.2	1.4	.14	.150	- .01
1.2	1.7	.17	.150	+ .02
1.5	2.0	.20	.187	+ .013
1.5	2.2	.22	.187	+ .033
2.0	2.5	.25	.250	.00
2.0	2.0	.20	.250	- .05
2.5	3.5	.35	.312	+ .038
2.5	3.0	.30	.312	- .012
3.0	4.0	.40	.375	+ .025
3.0	4.5	.45	.375	+ .075
3.5	5.0	.50	.438	+ .062
3.5	4.5	.45	.438	+ .012
4.0	5.0	.50	.500	- .000
4.0	6.0	.60	.500	+ .100
			Mean . . .	+ .012

TABLE V.

DETERMINATION OF MANGANESE BY THE LEAD PEROXIDE METHOD V.

Known $MnCl_2$ Solutions in Distilled Water Compared with $MnSO_4$ Standards. Treated in Same Manner in Original Beakers.

cc. $MnCl_2$	cc. $MnSO_4$ (Standard)	Milligrams of Manganese Found	Theory	Difference
0.0	0.00	.00	.00	.00
0.2	0.2	.02	.025	- .005
0.2	0.2	.02	.025	- .005
0.4	0.5	.05	.050	.00
0.4	0.4	.04	.050	- .01
0.6	0.7	.07	.075	- .005
0.6	0.6	.06	.075	- .015
0.8	1.2	.12	.100	+ .02
0.8	1.0	.10	.100	.00
1.0	1.4	.14	.125	+ .015
1.0	1.1	.11	.125	- .015
1.2	1.5	.15	.150	.00
1.2	1.4	.14	.150	- .01
1.5	2.0	.20	.187	+ .013
1.5	1.6	.16	.187	- .027
2.0	2.5	.25	.250	.00
2.0	3.0	.25	.250	.00
2.5	3.5	.35	.312	+ .038
2.5	3.0	.30	.312	- .012
3.0	4.0	.40	.375	+ .025
3.0	3.5	.35	.375	- .025
3.5	4.5	.45	.438	+ .012
3.5	4.0	.40	.438	- .038
4.0	5.0	.50	.500	+ .000
4.0	5.0	.50	.500	+ .000
			Mean . . .	- .002

TABLE VI.

DETERMINATION OF MANGANESE BY THE LEAD PEROXIDE METHOD VI.

Known $MnCl_2$ Solutions in Tap Water Compared with $MnSO_4$ Standards. Treated in Same Manner in Original Beakers.

cc. $MnCl_2$	cc. $MnSO_4$ (Standard)	Milligrams of Manganese Found	Theory	Difference
0.0	0.0	.00	.00	.00
0.2	0.2	.02	.025	- .025
0.2	0.2	.02	.025	- .025
0.4	0.5	.05	.050	.00
0.4	0.5	.06	.050	+ .01
0.6	0.7	.07	.075	- .005
0.6	0.8	.08	.075	+ .005
0.8	1.0	.10	.100	.00
0.8	1.0	.10	.100	.00
1.0	1.2	.12	.125	- .005
1.0	1.4	.14	.125	+ .015
1.2	1.5	.15	.150	.00
1.2	1.7	.17	.150	+ .02
1.5	2.0	.20	.187	+ .013
1.5	1.7	.17	.187	- .017
2.0	2.0	.20	.250	- .05
2.0	2.3	.23	.250	- .02
2.5	3.0	.30	.312	- .012
2.5	3.5	.35	.312	+ .038
3.0	3.5	.35	.375	- .025
3.0	4.0	.40	.375	+ .025
3.5	4.0	.40	.438	- .038
3.5	4.0	.40	.438	- .038
4.0	5.0	.50	.500	- .000
4.0	5.0	.50	.500	- .000
			Mean . . .	- .005

Chlorides, having a reducing action upon permanganates, also cause an error. In order to determine how serious the effect due to chlorides might be, series of determinations were made, in which evaporation with sulfuric acid was omitted, with 5, 10 and 25 milligrams of chlorine as NaCl added to tap water. The results, as shown in Table VII, indicate that when 5 milligrams were present, low results were always obtained. The mean deviation from the theoretical values is .016 milligrams. When 10 and 25 milligrams were present, no test whatever for manganese could be obtained. It is essential therefore that chlorine be removed for even when small amounts are present, serious errors are introduced. Chlorides in natural waters are very often present in amounts larger than those used in these experiments, and under these conditions manganese, if present, could not be detected unless the chlorine was first removed.

THE SODIUM BISMUTHATE METHOD

Schneider* appears to have first used bismuth

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*Dingl. poly. J., 269, 224. (1888).

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peroxide for the oxidation of manganous salts to permanganate. Other workers, however, found that the presence of chlorides in this oxide was deleterious and to overcome

TABLE VII.

DETERMINATION OF MANGANESE BY THE LEAD PEROXIDE METHOD VII.

In the Presence of 5 Milligrams of Cl as Chlorides.

cc. $MnCl_2$	cc. $MnSO_4$ (Standard)	Milligrams of Manganese Found	Theory	Difference
0.0	0.0	.00	.00	.00
0.2	0.2	.02	.025	- .005
0.2	0.2	.02	.025	- .005
0.4	0.3	.03	.050	- .02
0.4	0.4	.03	.050	- .02
0.6	0.5	.05	.075	- .025
0.6	0.6	.06	.075	- .015
0.8	0.7	.07	.100	- .03
0.8	0.9	.09	.100	- .01
1.0	1.1	.11	.125	- .015
1.0	1.2	.12	.125	- .005
1.2	1.2	.12	.150	- .03
1.2	1.4	.14	.150	- .01
1.5	1.8	.18	.187	- .007
1.5	2.0	.20	.187	+ .013
2.0	2.5	.25	.250	.000
2.0	2.0	.20	.250	- .05
2.5	3.0	.30	.312	- .012
2.5	3.0	.30	.312	- .012
3.0	3.5	.35	.375	- .025
3.0	3.5	.35	.375	- .025

this objection, Rammage and Reddrop* substituted sodium

*J. Chem. Soc., 67, 268. (1895).

bismuthate, which could be more easily obtained free from chlorides.

The method has been used widely for iron and steel analysis and has been shown to be accurate. It is described by Dufty,[1] Blair,[2] Blum,[3] Hillebrand and Blum,[4]

1. Chem. News, 84, 248. (1901)
2. J. Am. Chem. Soc., 26, 793-801. (1904)
3. Orig. Comm. 8th Intern. Cong. App. Chem., 61-85. (1912)
4. J. Ind. Eng. Chem., 3, 376. (1911)

and others.

Weston* first advocated it for use in water analysis.

*J. Am. Chem. Soc., 29, 1074-8. (1907)

Before this time, manganese was seldom determined in water. He describes the method giving some data which show it to be sufficiently accurate. The procedure for using this method as outlined in the 1912 edition of "Standard Methods of Water Analysis" is based upon Weston's work.

As used for the work described below, the procedure was essentially as follows. Varying amounts of the standard manganous chloride solution were diluted

with distilled water and with tap water. The portions were then evaporated with one or two drops of sulfuric acid (1:3) until white fumes appeared. Distilled water, dilute nitric acid and 0.5 gram of sodium bismuthate were then added, after which the samples were heated until the pink color disappeared. After allowing to partially cool, an excess of sodium bismuthate was added. The sample was stirred thoroughly, after which it was filtered thru a Gooch crucible previously prepared with asbestos, which had been washed, ignited and treated with potassium permanganate. The portions were then transferred to Nessler tubes and compared with standards prepared by,

1. Diluting standard potassium permanganate.
2. Treating standard manganous sulfate solutions like the samples.

The results obtained are shown in Tables VIII, IX, and X. Filtration thru asbestos does not seem to have any appreciable reducing effect upon the permanganate when sodium bismuthate is used as the oxidizing agent. This seems strange, for when lead peroxide was used, the effect was so great as to cause uniformly low values. The results indicate that the method is accurate under all the conditions here used. .01 milligram of manganese in a volume of 50 cc. can be detected by comparison in Nessler tubes.

In order to determine how seriously the results

TABLE VIII.

DETERMINATION OF MANGANESE BY THE BISMUTHATE METHOD I.

$MnCl_2$ Solutions in Distilled Water Compared with Diluted $KMnO_4$ Standards.

cc. $MnCl_2$	cc. $KMnO_4$ (Standard)	Milligrams of Manganese Found	Theory	Difference
0.0	0.0	.00	.00	.00
0.2	0.2	.02	.025	- .005
0.2	0.2	.02	.025	- .005
0.4	0.4	.04	.050	- .01
0.4	0.5	.05	.050	.00
0.6	0.7	.07	.075	- .005
0.6	0.7	.07	.075	- .005
0.8	1.0	.10	.100	.00
0.8	1.0	.10	.100	.00
1.0	1.2	.12	.125	- .005
1.0	1.2	.12	.125	- .005
1.2	1.5	.15	.150	.00
1.2	1.4	.14	.150	- .01
1.5	2.0	.20	.187	+ .013
1.5	1.7	.17	.187	- .017
2.0	2.5	.25	.250	.00
2.0	2.2	.22	.250	- .03
2.5	3.0	.30	.312	- .012
2.5	3.2	.32	.312	+ .008
3.0	3.5	.35	.375	- .02
3.0	4.0	.40	.375	+ .025
3.5	4.5	.45	.438	+ .012
3.5	4.5	.45	.438	+ .012
4.0	5.0	.50	.500	- .000
4.0	5.0	.50	.500	- .000
			Mean . . .	- .003

TABLE IX.

DETERMINATION OF MANGANESE BY THE BISMUTHATE METHOD II.

$MnCl_2$ Solutions in Distilled Water Compared with $MnSO_4$ .Standards Treated in the Same Manner.

cc. $MnCl_2$	cc. $MnSO_4$ (Standard)	Milligrams of Manganese Found	Theory	Difference
0.0	0.0	.00	.00	.00
0.2	0.2	.02	.025	- .005
0.2	0.2	.02	.025	- .005
0.4	0.4	.04	.050	- .01
0.4	0.5	.05	.050	.00
0.6	0.7	.07	.075	- .005
0.6	0.8	.08	.075	+ .005
0.8	1.0	.10	.100	.00
0.8	1.0	.10	.100	.00
1.0	1.2	.12	.125	- .005
1.0	1.1	.11	.125	- .015
1.2	1.5	.15	.150	.00
1.2	1.4	.14	.150	- .01
1.5	2.0	.20	.187	+ .013
1.5	2.0	.20	.187	+ .015
2.0	2.5	.25	.250	.00
2.0	2.5	.28	.250	+ .03
2.5	3.0	.30	.312	- .012
2.5	3.5	.35	.312	+ .038
3.0	3.5	.35	.375	- .025
3.0	4.0	.40	.375	+ .025
3.5	4.5	.45	.438	- .012
3.5	4.0	.40	.438	+ .035
4.0	5.0	.50	.500	- .000
4.0	5.0	.50	.500	- .000
			Mean . . .	+ .002

TABLE X.

DETERMINATION OF MANGANESE BY THE BISMUTHATE METHOD III.

$MnCl_2$ Solutions in Tap Water Compared with Diluted $KMnO_4$ Standards.

cc. $MnCl_2$	cc. $MnSO_4$ (Standard)	Milligrams of Manganese Found	Theory	Difference
0.0	0.0	.00	.00	.00
0.2	0.2	.02	.025	- .005
0.2	0.3	.03	.025	+ .005
0.4	0.5	.05	.050	.00
0.4	0.5	.05	.050	.00
0.6	0.8	.08	.075	+ .005
0.6	0.7	.07	.075	- .005
0.8	0.10	.10	.100	.00
0.8	0.08	.08	.100	- .02
1.0	0.12	.12	.125	- .005
1.0	0.11	.11	.125	+ .015
1.2	0.15	.15	.150	.00
1.2	0.15	.15	.150	.00
1.5	2.0	.20	.187	+ .013
1.5	1.8	.18	.187	- .007
2.0	2.5	.25	.250	.00
2.0	2.2	.22	.250	- .03
2.5	3.0	.30	.312	- .012
2.5	3.5	.35	.312	+ .038
3.0	4.0	.40	.375	- .025
3.0	4.0	.40	.375	- .025
3.5	4.5	.45	.438	+ .012
3.5	4.0	.40	.438	- .038
4.0	5.0	.50	.500	- .000
4.0	5.0	.50	.500	- .000
			Mean	- .004

were affected by chlorides, 5, 10, and 25 milligrams of chlorine as NaCl were added, omitting the evaporation with sulfuric acid. The determinations made under these conditions are shown in Table XI. The results indicate that in amounts of 5 milligrams or less, chlorine has no appreciable effect. When 10 milligrams or more are present the results are low. The effect of chlorides in the bismuthate method is much less pronounced than in the peroxide method where over 10 milligrams wholly prevented the appearance of any permanganate color.

The method is decidedly superior to the lead peroxide method. The permanganate color is not appreciably weakened by filtration thru asbestos. Color comparisons may therefore be made by filtering and transferring to Nessler tubes. Chlorides do not interfere so seriously as in the lead peroxide method. The fact that the permanganate is not so easily reducible in the presence of sodium bismuthate as in the presence of lead peroxide is probably due to the former reagent being a more active oxidizing agent than the latter. The results were found to be as accurate when the color comparisons were made with diluted potassium permanganate standards as when made with manganous sulfate solutions treated like the samples. The use of sodium bismuthate permits the detection of a slightly smaller amount of manganese than the use of lead peroxide.

TABLE XI.

DETERMINATION OF MANGANESE BY THE BISMUTHATE METHOD IV.

Known $MnCl_2$ Solutions in Distilled Water Containing Chlorides.

cc. $MnCl_2$	Theory	Milligrams of Manganese Found 5 mg.Cl.	Found 10 mg.Cl.	Found 25 mg.Cl.	Found 50 mg.Cl.
0.0	.0	.00	.00	.00	.00
0.2	.025	.02	.02	.00	.00
0.2	.025	.03	.02	.00	.00
0.4	.050	.05	.04	.03	.00
0.4	.050	.05	.03	.02	.00
0.6	.075	.08	.07	.05	.03
0.6	.075	.07	.08	.06	.04
0.8	.100	.10	.09	.08	.05
0.8	.100	.10	.10	.07	.05
1.0	.125	.12	.12	.10	.08
1.0	.125	.14	.12	.08	.10
1.2	.150	.15	.14	.14	.12
1.2	.150	.15	.13	.12	.10
1.5	.187	.20	.17	.15	.12
1.5	.187	.20	.15	.15	.15
2.0	.250	.25	.20	.20	.12
2.0	.250	.30	.25	.20	.20
2.5	.312	.30	.30	.25	.25
2.5	.312	.28	.32	.28	.20
3.0	.375	.35	.32	.30	.30
3.0	.375	.40	.32	.32	.25
3.5	.438	.45	.40	.40	.20
3.5	.438	.45	.35	.30	.20
4.0	.504	.50	.45	.37	.25
4.0	.504	.40	.45	.40	.20

THE PERSULFATE METHOD

The fact that persulfates oxidize manganous salts to permanganates in the presence of silver nitrate was first discovered by Marshall*. He suggested the reaction

*Chem. News, 83, 76. (1901)

as a qualitative test for manganese.

H. E. Walters* first used a modified form of the

*Chem. News, 84, 239. (1901)

method for the quantitative determination of manganese in iron and steel. After oxidizing the manganese to permanganate, the amount was found by titrating with arsenious acid. This method is now widely used in metallurgical work.

In water analysis, colorimetric comparison of the permanganate color is usually made instead of the volumetric titration. The method seems to be used by the majority of water analysts in preference to the lead peroxide and bismuthate methods. It has been advocated by Lührig and Becker,[1] Rodenberg,[2] Haas,[3] Schowalter,[4] Hartwig and Schellbach,[5] and Tillmans and Milder.[6] Most of these authors,

1. Pharm. Zenralhalle, 48, 137-42. (1907)
2. Chem. Weekblad, 7, 877-9. (1910)
3. Z. Nahr. Genussm., 25, 392-5. (1913); 27, 553-62. (1914)
4. Z. Nahr. Genussm., 26, 104. (1913)

5. Z. Nahr. Genussm., 26, 439-42. (1913)
6. J. Gasbel., 57, 496-501, 523-6, 544-7. (1914)

however, present no data as to the accuracy of the method.

In the work with the ammonium persulfate method described below, the procedure was as follows: Varying amounts of the standard manganous chloride solution were diluted with distilled water and with tap water to portions of about 50 cc. each. 2 cc. of nitric acid (1:1) and 5 cc. of silver nitrate solution (20 grams per liter) were added. After boiling and shaking the precipitate was filtered off. About 0.5 gram of ammonium persulfate crystals were added to the filtrate, and the solution was heated gently on the hot plate until the maximum permanganate color had developed, after which it was transferred to a 50 cc. Nessler tube. This color was compared with standards prepared by:

a. Diluting a standard potassium permanganate solution with water.

b. Diluting a standard manganous sulfate solution, and treating portions of this solution with nitric acid, silver nitrate, and ammonium persulfate, as in the case of the sample.

The results obtained by color comparisons according to these methods are given in Tables XII, XIII, XIV, and XV.

TABLE XII.

DETERMINATION OF MANGANESE BY THE PERSULFATE METHOD I.

Known $MnCl_2$ Solutions in Distilled Water Compared with Diluted $KMnO_4$ Standards.

cc. $MnCl_2$	cc. $KMnO_4$ (Standard)	Milligrams of Manganese Found	Theory	Difference
0.0	0.0	.0	.00	.00
0.2	0.2	.02	.025	- .005
0.2	0.3	.03	.025	+ .005
0.4	0.4	.04	.050	- .01
0.4	0.5	.05	.050	.00
0.6	0.7	.07	.075	- .005
0.6	0.7	.07	.075	- .005
0.8	1.0	1.0	.100	.00
0.8	1.1	1.1	.100	+ .01
1.0	1.2	1.2	.125	- .005
1.0	1.0	1.0	.125	- .025
			Mean . . .	- .004

TABLE XIII.

DETERMINATION OF MANGANESE BY THE PERSULFATE METHOD II.

Known $MnCl_2$ Solutions in Distilled Water Compared with $MnSO_4$ Standards Treated in the Same Manner.

		Milligrams of Manganese		
cc. $MnCl_2$	cc. $MnSO_4$ (Standard)	Found	Theory	Difference
0.0	0.0	.00	.00	.00
0.2	0.2	.02	.025	- .005
0.2	0.25	.025	.025	.00
0.4	0.6	.06	.050	+ .01
0.4	0.5	.05	.050	.00
0.6	0.7	.07	.075	- .005
0.6	0.8	.08	.075	+ .005
0.8	1.0	.10	.100	.00
0.8	1.1	.11	.100	+ .01
1.0	1.2	.12	.125	- .005
1.0	1.2	.12	.125	- .005
1.2	1.4	.14	.150	- .01
1.2	1.4	.16	.150	+ .01
1.5	1.8	.18	.187	- .007
1.5	1.8	.18	.187	- .007
2.0	2.4	.24	.250	- .01
2.0	2.5	.25	.250	.00
2.5	3.0	.30	.312	- .012
2.5	3.3	.33	.312	+ .018
3.0	3.5	.35	.375	- .025
3.0	3.8	.38	.375	+ .005
3.5	4.0	.40	.438	- .038
3.5	4.5	.45	.438	+ .012
4.0	5.0	.50	.500	- .000
4.0	4.5	.45	.500	- .050
			Mean . . .	- .004

TABLE XIV.

DETERMINATION OF MANGANESE BY THE PERSULFATE METHOD III.

Known $MnCl_2$ Solutions in Tap Water Compared with $MnSO_4$ Standards Treated in the Same Manner.

cc. $MnCl_2$	cc. $MnSO_4$ (Standard)	Milligrams of Manganese Found	Theory	Difference
0.0	0.0	.00	.00	.00
0.2	0.3	.03	.025	+ .005
0.2	0.2	.02	.025	- .005
0.4	0.5	.05	.050	.00
0.4	0.5	.05	.050	.00
0.6	0.7	.07	.075	- .005
0.6	0.7	.07	.075	- .005
0.8	0.9	.09	.100	- .010
0.8	1.0	.10	.100	.000
1.0	1.2	.12	.125	- .005
1.0	1.1	.11	.125	- .015
1.2	1.4	.14	.150	- .01
1.2	1.5	.15	.150	.00
1.5	1.8	.18	.187	- .007
1.5	1.9	.19	.187	- .007
2.0	2.5	.25	.250	.00
2.0	2.4	.24	.250	- .01
2.5	3.2	.32	.312	+ .008
2.5	3.3	.33	.312	+ .018
3.0	3.5	.35	.375	- .025
3.0	3.8	.38	.375	+ .005
3.5	4.5	.45	.438	+ .012
3.5	4.5	.45	.438	+ .012
4.0	5.0	.50	.500	- .000
4.0	4.7	.47	.500	- .030
			Mean	- .005

TABLE XV.

DETERMINATION OF MANGANESE BY THE PERSULFATE METHOD IV.

Known $MnCl_2$ Solutions in Tap Water Containing Chlorides Compared with $MnSO_4$ Standards Treated in the Same Manner.

Milligrams of Manganese

cc. $MnCl_2$	Theory	Found 50 mg.Cl.	Found 100 mg. Cl.	Found 200 mg.Cl.
0.0	.000	.000	.000	.000
0.2	.025	.02	.02	.02
0.2	.025	.02	.02	.02
0.4	.050	.04	.05	.04
0.4	.050	.05	.05	.05
0.6	.075	.07	.07	.08
0.6	.075	.08	.07	.08
0.8	.100	.11	.09	.10
0.8	.100	.10	.10	.10
1.0	.125	.12	.13	.12
1.0	.125	.12	.12	.12
1.2	.150	.14	.15	.16
1.2	.150	.16	.16	.15
1.5	.180	.18	.19	.17
1.5	.180	.20	.20	.19
2.0	.250	.22	.22	.25
2.0	.250	.25	.24	.25
2.5	.312	.30	.30	.32
2.5	.312	.28	.30	.30
3.0	.375	.35	.35	.40
3.0	.375	.40	.35	.40
3.5	.438	.45	.40	.45
3.5	.438	.45	.45	.50
4.0	.504	.50	.45	.55
4.0	.504	.50	.50	.50

precipitated with potassium chlorate from a one liter sample as manganese dioxide after concentration with nitric acid. The precipitated manganese dioxide is then dissolved in standard oxalic acid the excess of which is determined by titrating back with potassium permanganate. He states that the amount of manganese found must be increased by ten percent in order to give a correct value.

H. Noll* precipitates the manganese as manganese

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*Z. angew. Chem. 20, 490-2. (1907)

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dioxide in an ammoniacal solution with bromine water. This precipitate is then treated with hydrochloric acid and potassium iodide, and the liberated iodine is titrated with sodium thiosulfate. Results which were in good agreement with the theoretical values were obtained on some artificially prepared manganese waters. The volume of sample used was 500 cc.

These methods, however, have found little favor, and colorimetric methods are in general use.

All the colorimetric methods for the determination depend upon the oxidation of the manganous salt to permanganate and a comparison of the color thereby produced with standards of known permanganate content. Three oxidizing agents have been used for this oxidation. They are lead peroxide, PbO_2; sodium bismuthate, $NaBiO_3$; and

In the comparisons made with standards prepared by simply diluting potassium permanganate with water, it was found that amounts of manganese greater than .125 milligrams could not be compared easily on account of the difference in shade between the diluted permanganate standards and the samples. The potassium permanganate tubes were a reddish purple while the samples were a bluish purple. This was noticeable in all the concentrations used, but it did not cause great trouble except in amounts greater than .10 or .12 milligrams of manganese. In lower concentrations, accurate results were obtained as shown in Table XII. In the larger amounts the comparison was too unsatisfactory to be used.

When the standards were prepared by treating diluted solutions of manganous sulfate in the same manner as the samples, no difficulty was experienced in making the comparisons. The results (Tables XIII and XIV) show that the method is accurate. The series in which the manganous chloride solution was diluted with tap water gave as accurate results as were obtained with distilled water, the mean difference for the two series of twenty-five determinations being -.005 milligrams and -.004 milligrams, respectively.

The results show the desirability of using standards which have been oxidized with the persulfate reagent and treated in all respects like the samples. .005 milli-

gram of manganese in a volume of 50 cc. were easily detected under the conditions under which the test was carried on.

H. Lührig* states that high chlorides interfere

*Chem. Ztg., 38, 781-3. (1914)

in the persulfate method causing a blue color, and that iron interfers causing a reddish color.

In a series of determinations in which 50, 100, and 200 milligrams of chlorine as NaCl were present, the same accurate results were obtained. The data obtained are shown in Table XV. No bluish color was noted, and no difficulty was experienced in matching the colors. A large excess of silver nitrate and ammonium persulfate is to be avoided as it seems to produce a cloudiness, due perhaps to a precipitate of silver peroxide. Marshall* prepared silver per-

*Proc. Royal Soc. Edinburgh, 23, 163-8. (1900)

oxide by this method. It is very probable that the interference noted by Lührig* is due to this cause. Large amounts

*Loc. cit.

of iron must interfere on account of the yellow color of ferric salts. When manganese is present, the mixture pro-

duces the red color noted by Lüthrig.

In order to compare the three methods under working conditions, the manganese in several natural waters was determined by each method. The amounts found, together with the amounts of residue, chlorine, alkalinity, and iron, to show the character of the waters, are given in Table XVI. The samples were all taken below Streator from the Vermilion river which is polluted by coal mine drainage. The iron and chloride content is high. In the persulfate method, chlorides were precipitated with a slight excess of silver nitrate and filtered off. The final comparison was made with standards treated in the same manner as the sample. In the bismuthate method, evaporation of the sample with sulfuric acid was omitted. The final comparison was made with standards prepared by diluting the standard potassium permanganate solution. In the lead peroxide method the tests were made both with and without filtration thru Gooch crucibles, and both with and without evaporation with sulfuric acid. Standards were prepared by treating portions of the diluted manganous sulfate solution in the same manner as the samples.

The amounts found by the persulfate and the bismuthate methods agree very well. The amounts found by the lead peroxide method when carried out with chlorine removed and without filtering thru Gooch crucibles, also agree very well with those obtained in the persulfate and the bismuthate methods. When chlorine was not first removed,

TABLE XVI.

DETERMINATIONS OF MANGANESE IN NATURAL WATERS BY SEVERAL METHODS

(Results are stated in parts per million)

Lab. No.	Residue	Chlorine	Alkalinity	Iron	Manganese by Persulfate Method	Manganese by Bismuthate Method	Manganese by Lead Peroxide Method, Gooch Crucible, Chlorine Not removed	Manganese by Lead Peroxide Method, Gooch Crucible, Chlorine Removed	Manganese by Lead Peroxide Method, Decantation, Chlorine Not removed	Manganese by Lead Peroxide Method, Decantation, Chlorine Removed
29659	848	42	460	0.4	0.25	0.15	0.0	0.0	0.2	0.2
29660	2328	60	20	150.0	4.5	4.0	3.0	5.0	4.0	5.0
29661	2070	80	20	86.0	4.0	3.2	2.0	4.8	3.0	4.0
29662	2290	83	26	90.0	4.0	4.2	2.5	5.2	3.0	4.0
29663	2198	84	40	65.0	5.5	5.0	3.0	5.0	5.0	5.0
29664	2371	103	60	66.0	7.5	7.0	6.0	7.0	7.0	8.0
29665	2293	103	122	4.0	8.0	9.5	4.0	6.0	6.0	8.0
29666	345	25	144	0.2	0.0	0.0	0.0	---	0.0	---
29667	2396	102	90	46.5	9.0	8.5	6.0	7.0	8.0	7.0
29668	1591	17	92	126.5	1.4	1.4	0.6	1.6	1.0	1.5
29669	2660	65	200	57.5	2.0	1.8	1.8	2.0	2.0	2.0
29671	1970	92	4	48.0	4.0	4.0	2.0	6.0	3.0	4.0

however, the results were low, and when the Gooch crucible was used for the filtration, irregular results were obtained.

CONCLUSIONS

The persulfate method is the most convenient and accurate method for the colorimetric determination of manganese in water. Chlorides, being necessarily removed by precipitation, do not interfere. .005 milligrams of manganese in a volume of 50 cc. may be detected. The bismuthate method as outlined in the 1912 edition of "Standard Methods of Water Analysis" is accurate and reliable. In amounts of less than 5 milligrams, chlorine does not interfere, and unless the water is high in organic matter, evaporation with sulfuric acid may be omitted. .01 milligrams of manganese in a volume of 50 cc. may be detected.

The lead peroxide method as outlined in the 1912 edition of "Standard Methods of Water Analysis" gives results which are seriously low, due to permanganate reduction in using the Gooch crucible. When this step is omitted, more accurate results are obtained. Chlorides interfere in this method more seriously than in either of the others, and if more than 5 mg. of chlorine are present, no manganese whatever may be found even when a comparatively large amount is present. Evaporation with sulfuric acid is, therefore, necessary. .02 milligrams of manganese in a volume of 50 cc. may be detected by the decantation method. The peroxide

method is at best the least sensitive of the three, and it should be rejected as a standard method.

It seems advisable, therefore, to adopt as standard methods:

1. The Persulfate Method.
   a. Using colorless nitric acid.
   b. Omitting evaporation with sulfuric acid except when large amounts of organic matter are present.
   c. Comparison of the sample with standards prepared by treating manganous sulfate solutions exactly like the sample.

2. The Bismuthate Method.
   a. Using colorless nitric acid.
   b. Omitting evaporation with sulfuric acid except when more than 5 mg. of Cl or when much organic matter is present.
   c. Comparison of the sample with standards prepared either by treating standard manganous sulfate solutions exactly like the sample or by diluting a freshly prepared solution of potassium permanganate.

PART II.

MANGANESE IN ILLINOIS WATER SUPPLIES

The presence of manganese in water supplies, in concentrations great enough to be significant, has always been considered rather unusual. This is particularly true in the United States. In Europe, manganese has been encountered in water supplies in a number of instances.

R. S. Weston* cites some twenty ground water supplies in this country and in Europe which have been re-

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*Trans. Am. Soc. C. E. 64, 124. (1909)

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ported as containing manganese,

Locality	Manganese (Parts per million)
Arad, Hungary	present
Babylon, N. Y.	0.07
Bayshore, N. Y.	0.37
Berlin, Germany	present
Björnstorp, Sweden	3.4 - 53.4
Brunswick, Germany	present
Breslau, Germany	trace - 110.
Calverton, N. Y.	0.30
Halle, Germany	1.50
Hamburg, Hofbrünnen	0.45
Hanover, Germany	present
Patchogue, N. Y.	0.20
Reading, Mass.	0.004 - 0.56
Stargard, Germany	present
Stettin, Germany	5.22
Superior, Wisconsin	0.12
Shewsbury, Mass.	0.10

The first instance in this country where manga-

nese was reported present in sufficient quantity to cause trouble was in 1898*, in a well water supply of a New England

*Trans. Am. Soc. C. E. 64, 124. (1909)

mill. This supply was abandoned because of the high manganese content.

Sixty-two springs in the United States are listed by W. P. Mason* as having been reported to contain manganese.

*Chem. News, 61, 123. (1890)

Mason states that in nearly half of these there are only traces of the element, and only in seven instances did the amount equal or exceed the 4.5 parts per million which he found in a mineral spring at Excelsior Springs, Mo.

E. V. Raumer* reports a manganese bearing water

*Z. Anal. Chem. 42, 590-602. (1903)

near Fürth which contained 6.2 parts per million of the element.

E. H. S. Bailey* states that the well water supply

*J. Soc. Chem. Ind. 21, 681. (1902)

of Hutchinson, Ark., contains 1.0 part per million of manganese.

The water calamity of Breslau in 1906* is a classic example of injury to a water supply by a very

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*Z. öffent. Chem. 12, 121. (1906)
Z. öffent, Chem. 13, 401-11. (1907)
Z. Nahr. Genussm. 14, 40. (1907)
Z. prakt. Geol. 15, 153-64. (1907)
Chem. Ztg. 31, 255. (1907)
Trans. Am. Soc. C. E. 64, 174. (1909)

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high content of iron and manganese. Breslau was formerly supplied with water from the river Oder, but in 1905 a supply was substituted from 313 driven wells 30 to 40 feet deep in the Oder valley. In March, 1906, the Oder overflowed its banks, and soon afterward the turbidity, odor, hardness, residue, manganese, and iron in the ground water supply increased enormously. The iron content increased to 440 parts per million and the manganese content to 220 parts per million. The filtered water from the Oder river was necessarily substituted for the ground water supply. Many explanations have been offered for this peculiar change in the quality of the water. Most authorities agree that it was caused by a process of oxidation and leaching of the soil. The soil contains a large amount of iron and manganese sulfides. The iron sulfide was oxidized to iron sulfate by the dissolved oxygen of the river water.

The water containing iron sulfate then percolated thru the soil to the water bearing strata, a part hydrolyzing with the formation of sulfuric acid which dissolved the manganese and carried it along also. Extensive experiments on the removal of iron and manganese from the Breslau supply have been carried on by a number of investigators.

Manganese waters at Björnstorp Estate, Sweden, are described by M. Weibull.* Pipes were clogged, and

*J. Gasbel., 50, 767. (1907)

fabrics laundered in them were turned yellow by several waters from ponds and wells in the vicinity. Investigation showed that some of the waters contained as much as 0.3 parts per million of MnO, or 5 parts per million of Mn, which was precipitated upon exposure to the air. The rock formation in the vicinity is gneiss and diorite. The latter contains 8.2 percent MnO which probably accounts for the high manganese content of the waters of the vicinity.

A study of the manganese content of waters in France has been made by F. Jadin and A. Astruc.* In sev-

*Compt. Rendue 157, 538-9. (1913)

eral city supplies examined .0005 to .015 parts per million of manganese were found. Mineral waters at Vichy and Boulon

contained .09 to .20 parts per million. The manganese content varied widely in sources very near each other.

Prompted by the discovery of manganese in several Illinois city water supplies, an investigation was made to determine what relations, if any, exist between geological formation and manganese content, and to determine the source of the manganese in the water supplies. Accordingly, manganese, iron and dissolved solids were determined in a large number of samples selected from representative sources thruout the state.

Samples were taken from streams and wells, but only from those wells concerning which reliable information was available concerning the geological strata penetrated. Complete information of this kind concerning many private wells is not available. Rather complete logs of wells are usually kept of city wells. The majority of the supplies examined are, therefore, city water supplies. Samples were in all cases taken at the original sources, preliminary work having shown that manganese may separate out completely in the pipes before the water reaches distant taps.

METHODS OF ANALYSIS

The colorimetric persulfate method was used for the determination of manganese. The procedure was as follows.

Manganese

250 cc. of the sample were acidified with 2 cc. of nitric acid (1:1), and concentrated to a volume of less than 50 cc. If the sample was high in manganese, a smaller amount was used for the determination. The sample taken should not contain over .20 milligrams of Mn. Surface waters and, in general, waters showing a clay or silica-like turbidity were filtered before making the determination. After evaporation, the chlorides were precipitated with silver nitrate solution, a slight excess of the latter being used. The precipitate was filtered off. Samples which were very high in chlorides, were evaporated to white fumes with sulfuric acid after which distilled water and a small amount of silver nitrate solution were added. .5 gram of ammonium persulfate crystals were then added, and the solution was warmed until the maximum permanganate color had developed. Standards were prepared by taking portions of 0.2, 0.4, 0.6, etc., cubic centimeters of standard manganous sulfate solution, diluting to a similar volume and treating in exactly the same manner as the sample was treated. The sample and the standards were then transferred to 50 cc. Nessler tubes and the colors were compared. When the above procedure is followed the limit of detection is .02 parts per million.

Iron

Iron was determined either colorimetrically with potassium sulfocyanide or by permanganate titration after

fusing and dissolving the weighed oxides of iron and aluminum.

Dissolved Solids

Dissolved solids is the residue obtained by evaporating 100 cc. of the sample to dryness, heating the residue at 180° for one hour, and weighing. Samples having a clay or silica-like turbidity were filtered before evaporation. When the turbidity was due to precipitated ferric hydroxide, the sample was not filtered.

The supplies have been grouped as follows with reference to the source of water:

1. Wells in Potsdam sandstone.
2. Wells in St. Peter sandstone.
3. Wells in Limestone.
4. Wells in Drift.
5. Springs.
6. Coal mine drainage.
7. Lakes and Streams.

1. Wells in the Potsdam Sandstone.

Seventeen supplies from wells penetrating the Potsdam sandstone were examined. (See Table XVII.) In fourteen of these no manganese could be detected. A small amount was found in the other three, .08 parts per million in a well at Chicago, and .04 parts in wells at Riverside and Utica. These amounts are so small as to be of little significance. The iron content varies from .0 to 3.6

TABLE XVII.

MANGANESE, IRON AND DISSOLVED SOLIDS IN WATER FROM WELLS PENETRATING THE POTSDAM SANDSTONE.

Town	County	Depth	Manganese	Iron	Dissolved Solids
Aledo	Mercer	3165'	.00	0.0	2078
Amboy	Lee	2400'	.00	1.4	450
Aurora	Kane	2000'	.00	0.4	2198
Belvidere	Boone	1800'	.00	0.0	511
Blue Island	Cook	2000'	.00	0.2	1246
Byron	Ogle	2000'	.00	0.0	288
Carbon Hill	Grundy	1800'	.00	0.8	1295
Chicago*	Cook	2100'	.08	3.6	5520
Chicago*	"	1600'	.00	0.4	1057
Dixon*	Lee	1922'	.00	0.1	301
E. Dubuque	Jo Daviess	940'	.00	0.2	278
Forest Park	Cook	2015'	.00	0.0	530
Minonk	Woodford	1765'	.00	0.2	2337
Morrison	Whiteside	2048'	.00	0.5	293
Riverside	Cook	2000'	.04	0.2	891
Utica	LaSalle	350'	.04	0.5	444
Waukegan	Lake	1300'	.00	0.1	557

*Not public supply.

parts per million and the dissolved solids from 278 to 5520 parts. No relation is apparent between the manganese, iron and total mineral content.

The conclusion may be drawn that manganese is usually not present in water from wells in the Potsdam sandstone.

2. Wells in the St. Peter Sandstone.

Twenty-eight samples from wells penetrating the St. Peter sandstone were examined. (See Table XVIII.) Manganese was absent in all but one of them, that of a 1300-foot well at Elgin, which furnished a water containing .10 parts per million. This well is cased to a depth of only 100 feet, however, and the pumps were started for the purpose of taking the sample. Under these conditions it is very possible that water from some upper stratum also entered the well. The iron content of these supplies in the St. Peter sandstone varies from .0 to 4.0 parts per million, and the dissolved solids from 285 to 2977 parts. Manganese, then, is evidently usually absent from wells in the St. Peter sandstone. No relation appears to exist between the manganese, iron, and total mineral content.

3. Wells in Limestone.

Twenty-seven samples from wells penetrating limestone were examined. (See Table XIX.) Manganese is found in wells at Flora, Marion, Matteson, and San Jose', altho in no case is the amount over .08 parts per million.

TABLE XVIII.

MANGANESE, IRON AND DISSOLVED SOLIDS IN WATER FROM WELLS PENETRATING THE ST. PETER SANDSTONE.

Town	County	Depth	Manganese	Iron	Dissolved Solids
Abingdon	Knox	1350'	.00	0.0	1323
Bellwood	Cook	1400'	.00	1.0	546
Chadwick	Carroll	600'	.00	0.3	399
Chenoa	McLean	2100'	.00	1.1	1289
Cuba	Fulton	1765'	.00	0.4	2548
Elgin	Kane	1300'	.10	3.2	377
"	"	1300'	.00	0.4	493
Elmwood	Peoria	1300'	.00	0.7	1488
Farmington	Fulton	1465'	.00	0.3	1595
Galesburg	Knox	1240'	.00	0.0	1515
Genoa	DeKalb	1500'	.00	0.0	315
Henry	Marshall	1355'	.00	0.0	520
Ipava	Fulton	1575'	.00	0.0	2977
Jerseyville	Jersey	1542'	.00	0.1	3281
Kewanee	Henry	1485'	.00	0.3	1176
Lena	Stephenson	600'	.00	0.0	497
Oregon	Ogle	1600'	.00	0.8	285
Park Ridge	Cook	1425'	.00	1.0	820
Peru	LaSalle	1500'	.00	4.0	1730
River Forest	Cook	1000'	.03	0.1	452
Rochelle	Ogle	1026'	.00	0.1	337
Roseville	Warren	1260'	.00	0.0-1.4	566-2596
Rockdale*	Will	657'	.00	0.4	527
Spring Valley	Bureau	1400'	.00	0.1	770
Sycamore	DeKalb	905'	.00	2.2	340
Toulon	Stark	1465'	.00	0.0	1147
Warren	JoDaviess	865'	.00	0.1	379
Wyoming	Stark	1557'	.00	trace	1047

*Not city supply.

TABLE XIX.

MANGANESE, IRON AND DISSOLVED SOLIDS IN WATER FROM WELLS PENETRATING LIMESTONES.

Town	County	Depth	Manganese	Iron	Dissolved Solids
Anna	Union	650'	.00	0.0	347
Barrington	Cook	325'	.00	0.4	397
Carbondale	Jackson	410'	.00	0.1	2198
"	"	610'	.00	0.4	3395
Fairfield	Wayne	200'	.00	0.4	905
Flora	Clay	240'	.08	0.0	145
Forreston	Ogle	300'	.00	0.0	610
Highland Park*	Lake	395'	.00	0.0	490
Lake Forest*	Lake	242'	.00	0.2	255
Leland	LaSalle	230'	.00	4.8	337
Libertyville	Lake	128'	.00	0.1	712
Manteno	Kankakee	60'	.00	0.4	678
Marion	Williamson #1	700'	.04	0.6	1801
"	" #3	700'	.00	0.4	1110
"	" #4	700'	.04	0.2	1127
"	" #6	800'	.05	0.2	1562
"	" #7	960'	.06	0.3	1535
Matteson	Cook	283'	.04	4.0	713
Morris	Grundy	650'-800'	.00	0.0	434
Mt. Morris	Ogle	500'	.00	0.1	500
Pecatonica	Winnebago	20'	.00	0.1	336
San Jose'	Mason	105'	.08	0.0	539
Steger	Will	318'	.00	1.0	465
Trenton	Clinton	235'	.00	0.3	980
Villa Grove	Douglas	629'	.00	0.0	591
West Chicago	DuPage	322'	.00	0.8	405
North Crystal Lake	McHenry	285'	.00	0.3	344

*Not city supply.

Such small amounts are without practical significance. The iron content varies from .0 to 4.8 parts per million and the dissolved solids from 255 to 3395 parts. Manganese, then, is occasionally found in small amounts in water supplies from wells in limestone. It is usually absent, however, and when present the amount is too small to be of significance.

4. Wells in Drift.

Fifty-seven supplies from wells in the drift were examined. (See Table XX.) The drift may be divided into two classes, glacial and alluvial. Glacial drift represents the material deposited by the glaciers in their movement from the north over the state. Alluvial drift represents later deposits made by the deposition of the material carried down by the rivers. Careful logs of wells are necessary in order to determine whether or not wells near the large rivers are in glacial or are in alluvial drift. In any case, the mineral matter in water from wells in alluvium does not represent the mineral matter extracted only from the alluvium. The water from such wells is undoubtedly the result of the inflow of water from large areas of glacial material farther away. Very few of the drift wells examined penetrate the alluvium only, and in several cases the classification into glacial drift and alluvium wells could not be made with certainty from the data available. All the wells have, therefore, been called

TABLE XX.

MANGANESE, IRON AND DISSOLVED SOLIDS IN WATER FROM WELLS IN DRIFT.

Town	County	Depth	Manganese	Iron	Dissolved Solids
Arlington Heights	Cook	125'	0.00	0.2	751
Arthur	Moultrie	75'	0.00	2.2	491
Bement	Piatt	141'	0.04	1.5	547
Bloomington	McLean	100'	0.00	0.1	768
Braidwood	Will	20'	0.08	0.3	492
Camp Point*	Adams	40'	0.12	---	825
Canton *	Fulton	10'	1.10	0.6	194
Carlyle *	Clinton	25'	2.80	26.0	---
Champaign	Champaign	160'	0.00	2.0	389
Chillicothe	Peoria	35'	0.00	0.3	504
Crystal Lake	McHenry	32'	0.00	0.06	444
Danville*	Vermilion	150'	0.00	1.5	431
" *	"	150'	0.00	0.4	420
DuQuoin	Perry	30'	1.50	0.2	1066
Edwardsville *	Madison	55'-80'	0.5	1.8	252
Eureka	Woodford	90'	.08-.20	3.0	509-719
Freeport	Stevenson	40'	0.28	0.7	432
Gibson City	Ford	55'	0.04	0.1	320
Grand Ridge	LaSalle	196'	0.12	0.8	328
Greenview	Menard	80'	0.50	1.0	655
Havana	Mason	75'	0.08	0.0	202
Henry	Marshall	40'	0.00	0.0	518
Jacksonville	Morgan	#1 30'	0.00	1.7	515
"	"	#4 35'	0.00	2.0	424
"	"	#5 35'	0.00	1.8	372
Keithsburg	Mercer	35'	0.16	0.3	1262
Lacon	Marshall	50'	0.00	0.0	400
LaHarpe	Hancock	43'-63'	0.12	10.0	515
LaRose*	Marshall	28'	0.12	3.0	500
Lawrenceville*	Lawrence	30'	0.00	0.0	424
" *	"	15'	0.08	0.1	309
" *	"	30'	0.00	0.1	273
" *	"	11'	0.08	0.2	340
" *	"	13'	0.00	0.1	279
" *	"	20'	0.00	0.1	377
Lexington	McLean	115'	0.00	1.0	400
Lovington*	Moultrie	147'	0.08	1.3	548
Mansfield	Piatt	214'	0.04	2.1	390
Marengo	McHenry	14'	0.04	0.1	392
Mt. Sterling*	Brown	53'	0.28	0.3	698
Neoga	Cumberland	16'	0.00	0.0	299
Pekin	Tazewell	80'-128'	0.00	0.1	465

TABLE XX. (continued)

Town	County		Depth	Manganese	Iron	Dissolved Solids
Peoria	Peoria	#1	60'	0.16	0.0	394
"	"	#2	60'	0.44	0.0	303
"	"	#3	60'	1.60	0.1	302
"	"	#4	60'	0.75	0.8	270
"	"	#5	60'	0.75	0.6	289
"	"	#7	90'	0.08	0.0	413
Roanoke	Woodford		30'	0.06	0.9	900
Rushville	Schuyler		20'	0.24	0.2	362
Sheffield	Bureau		50'	0.20	0.1	505
Springfield	Sangamon		45'	0.60	2.0	325
Staunton	Macoupin		20'	0.12	0.0	325
Tolono	Champaign		140'	0.00	1.8	647
Urbana	"		160'	0.00	2.0	380
Washington	Tazewell		80'-90'	0.00	2.4	367
Woodstock	McHenry		85'	0.00	2.6	403

*Not city supply.

drift wells and no further separation into glacial and alluvial deposits has been attempted.

It will be noted that there is a very wide variation in the manganese content of these fifty-seven supplies, the range being from .0 to 2.8 parts per million. Twenty-one or thirty-four percent. contain more than .1 part per million of manganese, while nine, or sixteen percent. contain 0.5 or more parts per million.

The results obtained are plotted on the accompanying map. In the eastern half of the state, the drift wells contain little or no manganese. It is in the western part that the large amounts are found. The wells with the highest manganese content appear to be located near the rivers. For example, thirteen of the total number of wells contain more than .2 parts per million of manganese and ten of these are located either in the flood plains or terraces of rivers.

The total number of wells so located is seventeen, and these have been included in Table XXI. Twelve of the seventeen contain more than .2 parts per million of manganese. It seems, therefore, that wells in the drift near rivers are more likely to contain manganese than those located in other sections.

One rather striking fact is the great variation in the manganese content of five drift wells located very close to each other. These wells, 1, 2, 3, 4, and 5, are all within a few hundred feet of each other, and yet, the man-

MANGANESE
IN
ILLINOIS DRIFT WELLS
LEGEND
NONE
.00 - .10 P.P.M.
.10 - .50 P.P.M.
.50 + P.P.M.
Scale:
0 10 20 30 40 50 100 Miles
DAVIESS
STEPHENSON
WINNEBAGO
BOONE
MC HENRY
LAKE
CARROLL
OGLE
COOK
DE KALB
KANE
DU PAGE
WHITESIDE
LEE
KENDALL
ROCK ISLAND
HENRY
BUREAU
LA SALLE
WILL
GRUNDY
MERCER
PUTNAM
STARK
MARSHALL
KANKAKEE
HENDERSON
WARREN
KNOX
LIVINGSTON
PEORIA
WOODFORD
IROQUOIS
HANCOCK
MC DONOUGH
FULTON
TAZEWELL
MC LEAN
FORD
VERMILION
MASON
SCHUYLER
DE WITT
CHAMPAIGN
ADAMS
BROWN
CASS
MENARD
LOGAN
PIATT
MACON
SCOTT
MORGAN
SANGAMON
MOULTRIE
DOUGLAS
EDGAR
PIKE
CHRISTIAN
COLES
GREENE
SHELBY
CLARK
CALHOUN
MACOUPIN
MONTGOMERY
CUMBERLAND
JERSEY
EFFINGHAM
FAYETTE
JASPER
CRAWFORD
MADISON
BOND
CLAY
RICHLAND
LAWRENCE
CLINTON
MARION
ST. CLAIR
WAYNE
EDWARDS
WABASH
WASHINGTON
MONROE
JEFFERSON
HAMILTON
RANDOLPH
PERRY
FRANKLIN
WHITE
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TABLE XXI.

MANGANESE, IRON AND DISSOLVED SOLIDS IN WATER FROM WELLS IN DRIFT NEAR RIVERS.

Town	County	Depth	River	Manganese	Iron	Dissolved Solids
Carlyle	Clinton	25'	Kaskaskia R.	2.8	26.0	
Chillicothe	Peoria	35'	Illinois R.	0.00	0.3	504
Edwardsville	Madison	55-80'	Miss. R.	0.5	1.8	252
Freeport	Stevenson	40'	Pecatonica R.	0.28	0.7	432
Havana	Mason	75'	Illinois R.	0.08	0.0	202
Keithsburg	Mercer	35'	Miss. R.	0.16	0.3	1262
Lacon	Marshall	50'	Illinois R.	0.00	0.0	400
Peoria	Peoria	#1 60'	" "	0.16	0.0	394
"	"	#2 60'	" "	0.44	0.0	303
"	"	#3 60'	" "	1.60	0.1	302
"	"	#4 60'	" "	0.75	0.8	270
"	"	#5 60'	" "	0.75	0.6	289
"	"	#7 90'	" "	0.08	0.0	413
Canton	Fulton	10'	" "	1.10	0.6	194
Henry	Marshall	40'	" "	0.00	0.0	518
Rushville	Schuyler	20'	" "	0.24	0.2	362
Springfield	Sangamon	45'	Sangamon R.	0.60	2.0	325

ganese content varies from .16 to 1.6 parts per million. The other mineral constituents vary also. Specimens of borings from test wells in the vicinity of these manganese bearing waters were available. The percentages of manganese found in samples dried at 105° are shown in Table XXIII.

While no data concerning the normal manganese content of drift material are available, the manganese content of these samples does not seem unusual, but it may be sufficiently high to account for the occurrence of manganese in nearby water supplies.

No relation appears to exist between the manganese, iron and total mineral content of any of these waters.

5. Springs.

The ten spring waters examined show a very wide variation in manganese content. (See Table XXIII.) Six samples contained none, three contained between .3 and .4 parts per million, and one contained 7.8 parts per million.

This latter water from the Green Lawn Spring at Mt. Vernon, Illinois, has a higher manganese content than that of the spring at Excelsior Springs, Mo., which contains 4.5 parts per million as reported by Mason.* The

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*Chem. News, 61, 123. (1890)

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water containing no bicarbonates or free sulfuric acid, the iron and manganese occur as sulfates.

TABLE XXII.

THE MANGANESE CONTENT OF TEST WELL BORINGS

IN DRIFT

Well No.	Depth	Manganese percentage
2	0 - 8'6"	.21
7	3'6" - 18'	.30
78	0 - 5'	.57
78	5' - 8'6"	.46
78	8'6" - 19'5"	.56
78	19'5" - 24'2"	.31
119	0 - 5'6"	.46
119	5'6" - 7'6"	.22
119	7'6" - 9'	.23
119	21'7" - coal	.23

TABLE XXIII.

MANGANESE, IRON AND DISSOLVED SOLIDS

IN WATER FROM SPRINGS.

Town	County	Manganese	Iron	Dissolved Residue
Ashland	Cass	.00	1.8	490
Camp Point	Adams	.40	1.2	876
Harrisburg	Saline	.12	2.3	281
Jacksonville	Morgan	.00	0.0	378
Kewanee	Henry	.16	2.4	541
Oregon	Ogle	.00	0.5	402
"	"	.00	0.2	449
Mt. Vernon	Jefferson	7.80	51.2	1189
Sailor Springs	Clay	.00	3.4	1272
Taylorville	Morgan	.00	0.0	368

Note--None of these springs is used as a public water supply.

The fact is worthy of mention that a surface water at Mt. Vernon (see Table XXV) also contains from .12 to .80 parts per million of manganese. At Camp Point where the spring of next highest manganese content is found, we find a well water (see Table XX) containing .12 parts per million of manganese.

6. Coal Mine Drainage.

Coal mine drainage usually contains iron often in very large amounts. Such drainage is often acid, due to the hydrolysis of iron salts and the precipitation of iron hydroxide. Manganese has not been considered a constituent of mine water. An examination of six samples of coal mine drainage, however, shows that they all contain manganese, and some carry very large amounts. The analytical results are shown in Table XXIV. In one case the manganese content was as high as 56 parts per million. This sample contained free acid when analyzed. All contain large amounts of dissolved mineral matter, but none except the mine drainage from Harrisburg contains free acid. The occurrence of such large amounts of manganese in mine water has never been reported to our knowledge.

The source of iron in coal mine drainage is the iron sulfide minerals, pyrite and marcasite, and the sulfide shales which occur with the coal. The water containing dissolved oxygen leaches thru these minerals, and oxidizes the sulfides of iron to ferrous sulfate, thereby dissolving iron.

TABLE XXIV.

MANGANESE, IRON AND DISSOLVED SOLIDS

IN WATER FROM COAL MINES.

Town	County	Source	Manganese	Iron	Dissolved Solids
DuQuoin	Perry	Abandoned mine.	0.24	0.1	1160
Danville	Vermilion	Seepage from Stripping mine.	17.0	5.0	---
Harrisburg	Saline	Mine.	56.0	---	7339
Ladd	Bureau	Abandoned mine.	1.3	2.8	3144
Streator	LaSalle	" "	1.4	126.5	1379
"	"	Stobb's mine.	2.0	57.5	2245

It was thot that the manganese in water had a similar origin. Several samples of pyrite, marcasite, and shale from mines in the Streator district were examined for manganese. No trace of the element could be found in any of these, even when one-gram samples were used. A sample of sulfide shale, which occurs with the coal in the Stripping mine at Danville, where water containing 17 parts per million of manganese was found, was also examined. This was found to contain 1.10 percent of manganese. It seems very probable that manganese is leached from minerals by mine drainage in the same manner as iron.

7. Rivers and Lakes.

An examination of surface water supplies of the state shows that Lake Michigan and the large rivers are practically free from manganese. (See Table XXV.) None was found in any of the supplies obtained from Lake Michigan, while not over .02 parts were found in any of the supplies from the Mississippi, Ohio, Wabash, and Sangamon rivers. The Fox and Embarrass rivers contain only small amounts.

Some of the surface waters investigated, however, contain large amounts of manganese. The Vermilion river below Streator contains from 4 to 9 parts per million of manganese, and much larger amounts of iron, as shown by analyses of samples collected at Kangley, Lowell, and Oglesby. Samples taken at Streator above the water works

TABLE XXV.

MANGANESE, IRON AND DISSOLVED SOLIDS IN WATER FROM LAKES AND STREAMS.

Town	County	Source	Manganese	Iron	Dissolved Solids
Anna	Union	Reservoir on Kohler creek.	.0-7.5	.6-1.0	170-214
Belleville	St.Clair	Mississippi R.	0.02	0.1	234
Benton	Franklin	Reservoir on creek.	0.12	3.5	282
Cairo	Alexander	Ohio river.	0.00	0.1	150-240
Carlinville	Macoupin	Macoupin creek.	0.00	0.1	317
Centralia	Marion	Crooked creek.	0.20	0.1	---
Chicago	Cook	Lake Michigan	0.00	0.0	151
Danville	Vermilion	Vermilion R.	.00-.02	.0-.1	309-454
Decatur	Macon	Sangamon R.	0.00	.0-.1	305-375
E. St. Louis	St. Clair	Mississippi R.	0.02	0.1	230
Effingham	Effingham	Little Wabash R.	0.00	0.1	235
Evanston	Cook	Lake Michigan	0.00	0.0	158
Ft. Sheridan	"	" "	0.00	0.0	162
Glencoe	"	" "	0.00	0.0	155
Granite City	Madison	Mississippi R.	0.02	0.1	218
Greenup	Cumberland	Embarrass R.	0.00	0.05	681
Hamilton	Hancock	Mississippi R.	0.00	.0-.1	160-274
Harrisburg	Saline	Saline R.	0.32	0.3	671
Highland Park	Lake	Lake Michigan	0.00	0.05	140
Jacksonville*	Morgan	Morgan Lake	0.00	1.6	1041
Kankakee	Kankakee	Kankakee R.	0.04	0.1	377
Kangley*	LaSalle	Vermilion R.	4.00	150.0	2210
Kenilworth	Cook	Lake Michigan	0.00	0.0	192
Lake Forest	Lake	" "	0.00	0.0	177
Lawrenceville	Lawrence	Embarrass R.	0.02	0.1	575-1054
Lowell*	LaSalle	Vermilion R.	7.50	66.0	2316
Madison	Madison	Mississippi R.	0.02	0.1	224
Moline	Rock Island	" "	0.00	0.1	191
Mt. Carmel	Wabash	Wabash R.	0.00	0.1	300
Mt. Vernon	Jefferson	Reservoir	.12-.8	.1-.8	215-402
"	"	Casey Fork	0.00	0.1	155
North Chicago	Lake	Lake Michigan	0.00	0.0	164
Oblong*	Crawford	creek	0.36	1.0	1353
Olney	Richland	Fox river	0.04	0.7	145
Oglesby*	LaSalle	Vermilion R.	9.00	46.5	2323
Pontiac	Livingston	" "	.00-.08	.05-.2	447-557
Pullman	Cook	Lake Michigan	0.00	0.0	151
Quincy	Adams	Mississippi R.	.00-.02	0.1	222-250
Rock Island	Rock Island	" "	0.02	0.1	224
Staunton	Macoupin	Cahokia creek	0.16	0.1	550
Streator	LaSalle	Vermilion R.	0.00	0.0	848

TABLE XXV. (continued)

Town	County	Source	Manganese	Iron	Dissolved Solids
Venice	Madison	Mississippi R.	.02	.1	234
Waukegan	Lake	Lake Michigan	.00	.0	134
West Hammond	Cook	" "	.00	.0	146

*Not city supply.

dam, show no manganese and iron. This river, below Streator, is heavily polluted with mine drainage containing iron and manganese salts, which fact, explains the high manganese and iron content. The manganese content of .32 parts per million in the city supply of Harrisburg which is from the Saline river, is also due to the fact that the river above the city receives coal mine drainage of high manganese content.

Several surface waters, however, contain the element as one of their normal constituents. Impounding reservoirs on small creeks in southern Illinois frequently contain manganese. Among these are the supplies at Anna, Benton, Centralia and Mt. Vernon. Such reservoirs are fed partially by springs which may contribute the manganese. The manganese content of these supplies varies very widely. At Anna, a variation of from .2 to 7.5 parts per million over the period of nine months from July, 1914, to May, 1915, was observed. At Mt. Vernon, the variation was from .1 to .8 parts per million for the same period. The occurrence of such amounts of manganese in surface waters nearly saturated with dissolved oxygen is contrary to past conceptions of the occurrence of the element. In fact, much experimental work upon the removal of manganese has been based upon the theory that aeration oxidizes the manganous salt to an insoluble hydrated oxide which can be removed by filtration.

CONCLUSIONS

1. Manganese as a constituent of water supplies in the United States has been very much overlooked and its importance underestimated. It is a common constituent of certain classes of water supplies in Illinois, and in many cases, sufficient amounts are found to seriously affect the quality of the water. This may be said of the public water supplies at Mt. Vernon, Anna, Centralia, Peoria, Springfield, Freeport, and Harrisburg.

2. Manganese is not present in water supplies from wells in the Potsdam sandstone, the St. Peter sandstone and the limestones, nor in Lake Michigan and the large rivers.

3. Manganese is usually present and often in very large amounts in coal mine drainage.

4. Manganese is often present in water from:

   a. Impounding reservoirs on small streams in Southern Illinois.

   b. Drift wells near rivers.

No relation appears to exist between the manganese content of a water and any of the other mineral constituents, with the possible exception of coal mine drainage which contains manganese, and also a high iron content and much mineral matter.

PART III.

THE REMOVAL OF MANGANESE FROM WATER SUPPLIES

The experimental work which has been done upon the removal of manganese from water supplies has led to the development of three general methods.

1. Aeration and filtration thru sand.
2. Filtration thru Permutit.
3. Filtration thru pyrolusite.

The problem of manganese removal has been attacked by most workers in exactly the same manner as that of iron removal. The usual method for the removal of iron from water supplies is aeration followed by filtration thru sand. This method is in general and successful use in many plants in this country and in Europe. Iron occurs in natural waters in the ferrous condition. When the water is aerated, the iron is oxidized to the ferric condition and separates out as the hydroxide. This combined action of oxidation, hydrolysis and precipitation is the basic principle of the method, altho the presence of other substances in the water somewhat affects the results. The fact that manganese occurs oftentimes with iron, and that under certain conditions it separates out as the hydrated dioxide, has led to the assumption that the element when occurring in water has practically the same chemical properties as has iron.

Extensive experiments on manganese removal by this method have been carried on by Thiesing* who worked with

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*Mitt. kgl. Prüfungsans. Wasserversorgung (1912) 16, 210-96.

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a water at Pommerensdorf in Germany. He concludes that manganese occurring in water as the bicarbonate may be successfully removed by aeration and filtration. Trickling thru beds of coke or spraying thru nozzles were used as

methods of aeration. The reduction of carbon dioxide as well as the dissolving of oxygen was found to be important in the aeration process. Subsequent filtration thru sand gave an effluent of very low manganese content. Sedimentation effected very little removal.

In this country extensive experiments along similar lines, with several iron and manganese bearing waters in Massachusetts, have been carried on by R. S. Weston.* His work deals chiefly with the removal of iron.

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*Trans. Am. Soc. C. E., 64, 112-204. (1909)
J. N.E. Water Works Assn., 28, 27-59. (1914)

Three different supplies, located at Cohasset, Brookline, and Middleboro, were studied. At Cohasset a well water containing .73 parts per million of iron and .23 parts per million of manganese was treated by aeration by spraying thru nozzles followed by passage thru a coke trickler and mechanical filters. Satisfactory results were obtained. On the basis of the experiments, arrangements have been made for the construction of a large plant.

In experiments made at Brookline, aeration by sprinkling thru nozzles, followed by passage thru a coke trickler and slow sand filters reduced the iron from .6 parts per million to .2 parts per million. The manganese content of the untreated water was .26 parts per

million. The writer presents no figures concerning the efficiency of the manganese removal, but states that he found it to be roughly proportional to that of the iron removal.

At Middleboro, an iron and manganese removal plant has been installed which treats 335,000 gallons of water per day. The water is sprayed over a coke trickler 10 feet deep, allowed to run into a settling basin and finally thru slow sand filters operating at a rate of 10 million gallons per acre per day. The iron content was reduced from 1.5 to .2 parts per million and the manganese content from .67 to .27 parts per million during the first run from September 26, 1913, to January 12, 1914. The efficiency of the manganese removal increased as the plant was used for a longer time, and on January 22, the effluent contained .10 parts per million of manganese.

F. A. Barbour* has performed a similar series of

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*Eng. News, 70, 78-9. (1914)

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experiments on the well water supply of the city of Lowell, Mass. The several wells used vary in manganese content, the highest being 2.0 parts per million. Aeration, sedimentation and subsequent sand filtration was used on an experimental scale. The efficiency of the plant was at first rather

erratic, but it finally became possible to reduce the manganese content to .01 part per million. A dark coloration due to precipitated oxides of manganese was observed in the sand bed, and this extended in a diminishing amount to the bottom of the bed. On the basis of this work, a large plant to cost $180,000 is now being erected for the removal of the manganese and iron. It is expected that the plant will be completed in the fall of 1915.

To sum up the work on manganese removal by aeration and filtration, it may be said that all workers conclude that manganese is much more difficult to remove than iron. The details of the process, such as the amount of aeration and the rates of filtration necessary, vary with the character of the water.

A second method for manganese removal which has come into the field recently is the Permutit process. Permutit, the artificial zeolite first produced and patented by Robert Gans* of the Prussian Geological Institute of

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*Chemical Review. Felt-Harz Ind. 16, 302-3.
Original Comm. 8th Int. Cong. App. Chem. 25, 125. (1912)
Chem. Ind. 32, 197-200. (1909)

Berlin, has come into somewhat common use in water softening. Its use for the purpose of removing calcium and magnesium salts from water has been studied by a large number of investigators. Gans, however, has adapted it

to the removal of manganese from water supplies. The principles involved in this latter process are decidedly different from those involved in ordinary water softening.

Sodium Permutit is made by fusing together 3 parts of kaolin, 6 parts of sand and twelve parts of soda. The melt, after cooling, is leached with water. Gans* proposès the following formula to represent sodium Permutit.

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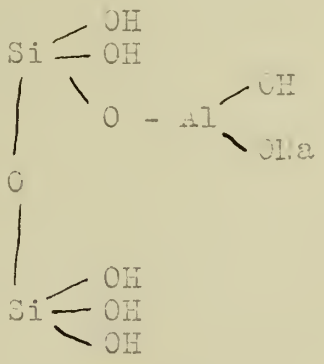
*Chem. Ind. 32, 197-200. (1909)



The sodium in this compound is replaceable by other metals. For example, when a solution of a calcium salt is allowed to percolate thru the crushed material, the calcium replaces the sodium in the silicate, is removed from the solution and in turn is replaced by an equivalent of sodium.

On the other hand, a solution of a sodium salt may be filtered thru the calcium permutit and the calcium

forced out by the sodium. The process may be simply represented by the equilibria:

$$Ca^{++} + 2Na\text{-Permutit} \rightarrow 2Na^{+} + Ca\text{-Permutit}.$$

$$Mg^{++} + 2Na\text{-Permutit} \rightarrow 2Na^{+} + Mg\text{-Permutit}.$$

It can readily be seen how a hard water can be made to percolate thru sodium Permutit, and the calcium and magnesium ions in the water be replaced by the sodium ion. After this change is complete, a sodium chloride solution is made to percolate thru the used Permutit and the calcium and magnesium therein are in turn removed and replaced by sodium. The Permutit is thus returned to its original condition without loss, the process being spoken of as regeneration. The whole constitutes a very nice application of the law of mass action. Permutit is not lost unless the water contains free carbon dioxide, the latter having a solvent action on the Permutit due to the formation of bicarbonates.

Gans* noted that manganese could be removed with the calcium and magnesium salts when a manganese

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*Chem. Ztg. 31, 355-6. (1907)

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bearing water is filtered thru the zeolite. In most cases, however, it is desired to remove only the manganese without the extra expense of softening the water.

To accomplish this, Gans* treated his Permutit

*Chem. Ind. 33, 48-51; 66-9. (1910)

with a strong solution of manganous chloride or sulfate, and then with a strong permanganate solution. Upon filtering a manganese or an iron bearing water thru this medium, he found that the manganese and iron could be removed without the accompanying softening action. After a time the filter medium no longer effected removal, but upon regenerating with permanganate, its efficiency was restored.

The chemistry of this process is explained by Gans*

*Loc. cit.

as follows. The first treatment with manganous chloride gives a manganese zeolite.

$$2SiO_2 \cdot Al_2O_3 \cdot CaO + MnCl_2 \rightarrow 2SiO_2 \cdot Al_2O_3 \cdot MnO + CaCl_2$$

When this zeolite is treated with permanganate, the following reactions may take place.

a. $2SiO_2 \cdot Al_2O_3 \cdot MnO_2 + CaMn_2O_8 \rightarrow 2SiO_2 \cdot Al_2O_3 \cdot CaO + MnO \cdot Mn_2O_7$

b. $2(SiO_2 \cdot Al_2O_3 \cdot MnO) + H_2O + CaMn_2O_8 \rightarrow \begin{matrix}(2SiO_2 \cdot Al_2O_3 \cdot CaO) \\ (2SiO_2 \cdot Al_2O_3 \cdot H_2O)\end{matrix} + 2MnO \cdot Mn_2O_7$

c. $3(SiO_2 \cdot Al_2O_3 \cdot MnO) + 2H_2O + CaMn_2O_8 \rightarrow \begin{matrix}(2SiO_2 \cdot Al_2O_3 \cdot CaO) \\ (2SiO_2 \cdot Al_2O_3 \cdot H_2O) \\ (2SiO_2 \cdot Al_2O_3 \cdot H_2O)\end{matrix} + 3MnO \cdot Mn_2O_7$

The precipitation of manganese by these zeolites depends upon the action of the oxides of manganese, and is represented by the following reactions.

a. $2(MnO \cdot Mn_2O_7) + 2Mn(HCO_3)_2 \rightarrow 5MnO \cdot 2Mn_2O_7 + 6CO_2 + 2H_2O$

b. $2MnO \cdot Mn_2O_7 + 3Mn(HCO_3)_2 \rightarrow 5MnO \cdot Mn_2O_7 + 6CO_2 + 3H_2O$

c. $2(3MnO \cdot Mn_2O_7) + 9Mn(HCO_3)_2 \rightarrow 15MnO \cdot 2Mn_2O_7 + 18CO_2 + 9H_2O$

Gans* applied the process with complete success

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*Oesterr. Chem. Tech. Ztg. 26, Bohrtechnicker section 15, 178.

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to a water at Glogau containing 1.5 to 2.0 parts per million of manganese. The free carbon dioxide was first removed by passing the water thru crushed marble. The treated water was free from manganese and neutral. The hardness was increased slightly, due to the solution of calcium in the neutralization of free carbon dioxide. In the process, iron is removed with the manganese. The cost of the installation of the Permutit process is high, and it has been introduced in few cases for large scale operations.

In the recent advertising literature put out by The Permutit Company in the form of a pamphlet, entitled, "The Chemistry of Permutit," the oxide, Mn_2O_7 is considered as the basis of the removal process. The reactions presented are as follows, the letter p representing Permutit.

$$p\text{-}Na_2 + MnCl_2 = p\text{-}Mn + 2NaCl$$

$$p\text{-}Mn + 2KMnO_4 = p\text{-}K_2MnO\cdot Mn_2O_7$$

$$p\text{-}K_2MnO\cdot Mn_2O_7 = p\text{-}K_23MnO + 50$$

In this discussion, the question of whether the reduction is to MnO, MnO_2, or Mn_2O_3 is considered to be undecided.

The third method of manganese removal was brought out by A. Pappel* in the form of a patent. In the process,

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*German Patent, 241,571, Aug. 22, 1908.
Chem. Ztg. 36, Rep. 7. (1912)

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the manganese bearing water is filtered thru granular pyrolusite. The material finally may lose its power of removal, but the power is restored by washing with ordinary tap water.

This process was later investigated experimentally at the city of Dresden by R. Schmeitzner.* It was not,

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*Techn. Gem. kl. 15, 343.
Wasser u. Abwasser 7, 376-7.

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however, adopted there for use on a large scale.

Manganese is removed from the city water supply of Breslau by this method. A natural sand containing pyrolusite is used as the filter medium.

J. Tillmans and O. Heublein* have studied the

*Z. Nahr. Genussm. 27, 253-64. (1914)

theory of manganese removal by this method. By suspending pieces of pyrolusite in tubes containing a solution of manganous sulfate solidified with gelatine, allowing it to stand and then pouring ammonia on the surface, they noticed an absence of the Liesegang rings in the vicinity of the pieces of pyrolusite. The power of this substance to absorb and remove manganous salts from solutions was thus shown. When pure MnO_2 was allowed to act on a dilute $MnSO_4$ solution, it was found that the free acid formed was e uivalent to the manganese removed. They consider the reaction to be:

In a later article, Tillmans* reviews his former

*J. Gasbel. 57, 713-24. (1914)

work, and states that manganese dioxide is the essential medium which removes manganese in the Permutit process.

In addition to these methods for the removal of manganese, others have been proposed in which chemicals to precipitate the element are added to the water.

Lürhrig and Blasky*, who were among the first to experiment

*Chem. Ztg. 31, 255. (1907)

upon this problem, suggested the addition of potassium permanganate or lime to precipitate the manganese. These chemical methods have not come into practical use.

We undertook a study of the methods to determine the chemistry of the processes and especially the one in which the water is treated by aeration.

Manganese Permutit.

Specimens of manganese Permutit were kindly furnished by The Permutit Company for the work.

The material consists of irregular, black grains about 2 or 3 millimeters in diameter. When these are crushed, a white core is noted in the center of each. A specimen of the Permutit was ground, dried at 105°, and analyzed. Manganese was determined as pyrophosphate. Available oxygen was determined by distilling the chlorine evolved on treatment with hydrochloric acid into potassium iodide, and titrating the liberated iodine. The analysis obtained is as follows.

Potassium oxide,	K_2O	4.00
Sodium oxide,	Na_2O	4.37
Calcium oxide,	CaO	1.87
Magnesium oxide,	MgO	.17
Ferric oxide,	Fe_2O_3	.42
Alumina,	Al_2O_3	22.72
Silica,	SiO_2	38.28
Manganous oxide,	MnO	10.37
Available Oxygen,	O	1.94
Water,	H_2O	15.34
	Total	99.48

This specimen of Permutit had been prepared by treating a sodium Permutit with a manganous salt, and afterward with potassium permanganate. The amount of manganese found, calculated as MnO is 10.37 per cent., while the amount of available oxygen which should determine the degree of oxidation of the manganese was found to be 1.94 per cent. The theoretical amount of available oxygen which should have been obtained had the manganese been present in each form is as follows:

	Available O.
For 10.37 percent. MnO as MnO_2 - -	2.37
" 10.37 " " " Mn_2O_3 - -	1.17
" 10.37 " " " Mn_3O_4 - -	0.78
" 10.37 " " " MnO - -	none

As 1.94 per cent. available oxygen was actually found, it is clear that the oxide is higher than MnO, Mn_3O_4, and Mn_2O_3, but not so high as MnO_2.

In order to determine what compounds of manganese effected the removal, specimens of the ground manganese Permutit were regenerated to the highest possible degree, and reduced to the lowest possible degree.

One portion was treated with a saturated solution of $KMnO_4$, placed in a shaking machine, and agitated for several days. It was then allowed to stand for two weeks longer. At the end of this time, the solid material was filtered off, washed free from permanganate, dried and analyzed. The composition was as follows:

Potassium oxide,	K_2O	10.26
Sodium oxide,	Na_2O	1.00
Calcium oxide,	CaO	1.28
Magnesium oxide,	MgO	trace
Ferric oxide,	Fe_2O_3	0.66
Alumina,	Al_2O_3	22.62
Silica,	SiO_2	39.09
Manganous oxide,	MnO	12.30
Available oxygen,	O	2.49
Water,	H_2O	10.83
	Total	100.53

The empirical formula of the substance calculated from the above analysis is:

$$3R_2O \cdot 3MnO_x \cdot 4Al_2O_3 \cdot 12SiO_2 \cdot 11H_2O$$

R_2O representing the oxides of the alkalies and alkaline earths.

After regeneration, the amount of manganese calculated to MnO was found to be 12.30 percent., and the available oxygen 2.49 percent. The theoretical amount of available oxygen, had all the manganese been in the form of MnO_2, would have been 2.77 per cent. This shows that regeneration has increased the available oxygen ratio or the degree of oxidation of the manganese, but that it is still

somewhat lower than the theoretical for MnO_2.

There are several reasons why a lower available oxygen content than the theoretical might be obtained. The treatment may not have been continued sufficiently long to complete the reaction. It is very probable that all the manganese which is present in an insoluble silicate of this character cannot be reached and attacked by the permanganate, owing to the physical structure of the material. Moreover, Morse, Hopkins and Wheeler* have shown that

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*Am. Chem. J. 18, 401-19. (1896)

MnO_2 loses a small amount of its oxygen upon drying in the air, and that compounds such as $MnO \cdot 50MnO_2$ are obtained. For this reason, an available oxygen content slightly lower than that actually present would be found by the analysis as carried out.

Of particular interest in this specimen is the large percentage of potassium and the small percentages of sodium, calcium and magnesium compared with the smaller percentage of potassium and the larger percentages of sodium, calcium and magnesium found before regeneration. This is explained by the fact that these metals are replaceable, and that treatment with potassium permanganate has not only brought about the oxidation of the manganese, but at the same time has effected a replacement of the other metals with potassium.

The replacement effect could be represented graphically by the reaction,

$$(K,Na,Ca)\ \text{Permutit} + 3K^{+}\ MnO_4^{-} \rightarrow K_x\text{Permutit} + Ca^{++}(MnO_4^{-})_2 + NaMnO_4$$

Coincident with the replacement, the oxidation of the manganese in the zeolite takes place, giving manganese dioxide as the limit of oxidation, and not such higher oxides as $MnO \cdot Mn_2O_7$ and $2MnO \cdot Mn_2O_7$, as suggested by Gans.*

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*Loc. cit.

A portion of this regenerated sample was then shaken with a strong solution of manganous sulfate in the same manner. After washing and drying it was found to have the composition shown below.

Potassium oxide,	K_2O	3.15
Sodium oxide,	Na_2O	2.20
Calcium oxide,	CaO	0.54
Magnesium oxide,	MgO	trace
Ferric oxide,	Fe_2O_3	0.50
Alumina,	Al_2O_3	23.05
Silica,	SiO_2	38.37
Manganous oxide,	MnO	15.05
Available oxygen,	O	2.00
Water,	H_2O	14.76
	Total	99.62

The empirical formula calculated from this analysis would be,

$$1\ 1/2\ R_2O \cdot 4MnO_x \cdot 4Al_2O_3 \cdot 12SiO_2 \cdot 16H_2O$$

The amount of available oxygen was found to be 2.00 per cent. The theoretical available oxygen for Mn_2O_3, the oxide next lower than MnO_2, would be 1.70 per cent. It was subsequently found, however, that in the analysis of the reduced material, oxygen was taken up while the substance was being dried in the air. The content of 2.00 percent., therefore, is probably high, and little significance should be attached to it.

The low percentage of sodium and potassium, and the high percentage of manganese is of interest, especially when compared with the corresponding figures for the regenerated specimen. The explanation lies in the fact that here, again, there has been a replacement as well as a reduction.

The replacement is the substitution of manganese for the sodium and potassium of the Permutit. This could be represented by the reaction,

$$K_2\text{Permutit} + \overset{++--}{MnSO_4} \rightarrow \text{Mn Permutit} + \overset{+\ --}{K_2SO_4}$$

The extent to which this reaction takes place is governed by the concentration of manganese in the solution. As the amount is very low in practice, it must take place to only a very slight extent.

At the same time there is a reduction of the manganese dioxide to a lower oxide by the manganous salt. This may be represented graphically as follows,

$$MnO_2 + MnSO_4 \rightarrow Mn_2O_x + SO_3$$

The latter effect is the basic reaction involved in the Permutit process.

The acid which is formed from the reaction when the manganese is removed is undoubtedly neutralized by the alkaline silicate, it having been shown by Gans* that free

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*Loc. cit.

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acid, even carbonic acid, has a solvent action on the Permutit.

Summarizing, it may be said that manganese Permutit consists of a zeolite with which is incorporated a layer of manganese dioxide. When a manganese bearing water is filtered thru this medium, the manganese is removed by the formation of a lower oxide of manganese. The lower oxide is formed from a reaction between the manganous salt and manganese dioxide. There is at the same time a replacement of the alkali or alkaline earth metal of the silicate by the manganous salt present in the water. The replacement is of very minor practical importance, and the slight extent to which it takes place is dependent upon the concentration of manganese in the water.

When the manganese Permutit is regenerated with potassium permanganate, manganese is added to the Permutit. When manganese is removed from water by the regenerated

Permutit, manganese is also added to the Permutit. Therefore, with each successive regeneration and reduction, the manganese dioxide content increases, and the filter medium tends to approach in composition pure manganese dioxide. The zeolite cannot increase in amount with successive reduction and regeneration, and the replacement effect must, therefore, become less and less as the substance is used.

These results are in entire accord with the conclusions reached independently by Tillmans* that the

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*J. Gasbel. 57, 713-24. (1914)

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action of manganese Permutit is really the action of manganese dioxide.

Sand Filtration.

Some preliminary experiments made by filtering an aerated, artificially prepared, manganese bearing water thru a small sand filter showed that no manganese removal was obtained. At Mt. Vernon, Illinois, however, a mechanical filtration plant has been installed for the purpose of removing manganese as well as effecting hygienic purification of a surface water. Analyses of the water made some months after the installation of the mechanical filters showed that manganese was being removed by this plant. At Anna, Illinois, manganese is also removed in a filter plant designed for the

purpose of hygienic purification of a surface water supply. These results seemed contradictory to the negative results obtained on a small scale.

As manganese dioxide had been used successfully for manganese removal, and as this compound is the basic part of manganese Permutit, it was thot that in successful sand filtration methods manganese dioxide was probably the principal factor in the removal.

Two filters were, therefore, prepared for experimental purposes. The apparatus (See Fig. 1) consisted of two gas washing cylinders (A, A) connected at the top by a syphon to a large carboy (B) holding the water to be treated. By the use of two stop cocks (S, S) the rate of filtration could be varied and so adjusted that both filters delivered their effluents at the same rate. A glass tube (C) extending to the bottom of the carboy provided means for admitting compressed air for aeration.

Both filters were filled with exactly one liter of a clean, high grade filter sand, having an effective size of .50 mm. and a uniformity coefficient of 1.32. One of these filters was treated alternately with solutions of manganous sulfate, sodium hydroxide, and potassium permanganate. After two or three treatments, a thin film of black oxide of manganese had formed on the sand grains. The filter was then washed with water until an effluent free from manganese was obtained. The other

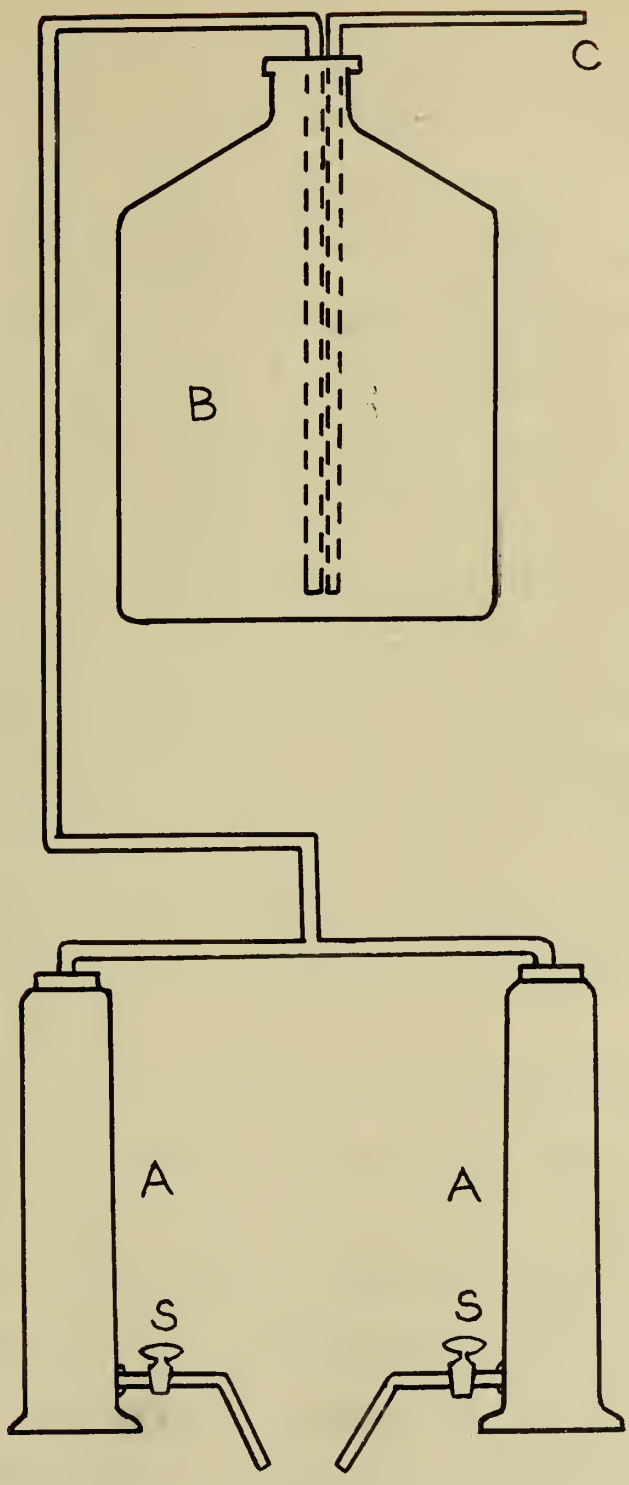

Figure 1.

filter was used with no treatment. The apparatus consisted, then, of two filters working in parallel, one containing sand only, and the other, sand which had been slightly coated with manganese dioxide. The volume of sand in each was one liter, the depth was 35 centimeters, and the area was therefore 28 square centimeters.

In a manganese removal filter, the removal depends upon the contact of the manganous salt with manganese dioxide, as the data presented later will show. Consequently, the rate of filtration should be expressed in terms of volume of water filtered per volume of filter medium, and not per area of filter surface. In these experiments the rate varied slightly, but was so adjusted that a volume of water equal to the volume of filter medium was filtered in twenty minutes. Samples were taken at intervals for analysis.

The water used was prepared by dissolving the necessary salts to be added, iron and manganese, either in tap water, distilled water, or a mixture of the two. The tap water is a bicarbonate, iron-bearing water from drift wells. The following determinations which are of significance in a discussion of manganese removal will represent the character of the tap water used.

	Parts per million
Turbidity	5.
Color	15.
Residue on evaporation	370.
Chlorine	.3
Alkalinity to Methyl Orange	355.
Free Carbon Dioxide	40.
Iron	2.0
Manganese	none
Hardness	300.
Dissolved oxygen	none
Oxygen Consumed	4.8

The first artificial water used was prepared by mixing tap water and distilled water in about equal parts. 5 parts per million of manganese as $MnSO_4 \cdot 4H_2O$ were added. The water was aerated by blowing air thru it for one hour and allowing to stand for two hours. It was then filtered thru the apparatus, and determinations of manganese, iron, carbon dioxide, dissolved oxygen, and alkalinity, were made in samples taken at two hour intervals. The results are shown in Table XXVI.

Aeration has decreased the free carbon dioxide to a content of from 2 to 4 parts per million, and increased the dissolved oxygen content to 7.4 parts per million. Filtration thru the sand filter has removed practically all of the iron, but it has caused practically no change in the manganese, dissolved oxygen and alkalinity. Filtration thru the sand coated with manganese dioxide, on the other hand, has removed all manganese and iron, has reduced the dissolved oxygen content an average of

TABLE XXVI.

MANGANESE REMOVAL BY AERATION AND FILTRATION

(Results are stated in parts per million)

At Start	Unfiltered	Filtered thru	
		Sand	Sand coated with MnO_2
Manganese	4.8	4.4	0.0
Iron	0.4	0.05	0.0
Alkalinity	200.0	200.0	196.0
Dissolved oxygen	7.4	7.2	6.2
Carbon dioxide	4.0	2.0	2.0
Two hours			
Manganese	4.8	4.8	0.0
Iron	0.4	0.05	0.0
Alkalinity	200.0	200.0	194.0
Dissolved oxygen	7.2	7.4	6.6
Four hours			
Manganese	4.8	4.4	0.0
Iron	0.4	0.05	0.0
Alkalinity	200.0	200.0	194.0
Dissolved oxygen	7.4	7.4	6.6
Carbon dioxide	2.0	4.0	6.0
Six hours			
Manganese	4.8	4.0	0.05
Iron	0.4	0.05	0.0
Alkalinity	200.0	200.0	192.0
Dissolved oxygen	7.5	7.5	6.8

.8 parts per million and the alkalinity an average of .4 parts per million. These results indicate that aeration and sand filtration do not remove appreciable amounts of manganese. The reaction in the manganese dioxide filter may be explained as follows. The manganous salt evidently combines with manganese dioxide to form a lower oxide exactly as in the pyrolusite and the Permutit processes. When manganese is removed, an equivalent of free acid is of course formed which causes a corresponding reduction in the alkalinity. This reduction should theoretically be 10 parts per million when 5 parts per million of manganese are removed, whereas the actual reduction was only 4 parts per million. The disappearances of .8 parts per million of dissolved oxygen in the manganese dioxide filter is undoubtedly due to the oxidation of the lower oxide of manganese back to manganese dioxide. If this were quantitative, the removal of 5 parts of manganese should reduce the dissolved oxygen content 1.6 parts. The actual reduction was only .8 parts, however.

In another series of experiments, tap water was used, in which ten parts per million of manganese as $MnSO_4 \cdot 4H_2O$ had been dissolved. The results are shown in Table XXVII.

In general, these results obtained with a water containing ten parts per million of manganese are similar to those obtained in the former series. Filtration thru

TABLE XXVII.

MANGANESE REMOVAL BY AERATION AND FILTRATION

(Results are stated in parts per million)

At Start	Unfiltered	Filtered thru	
		Sand	Sand coated with MnO_2
Manganese	10.5	9.0	0.1
Iron	0.8	0.0	0.0
Alkalinity	356.	354.	342.
Dissolved oxygen	5.3	3.4	5.0
Carbon dioxide	4.	6.	8.
Two hours			
Manganese	10.	10.5	0.1
Iron	0.8	0.0	0.0
Alkalinity	358.	356.	344.
Dissolved oxygen	5.6	4.2	4.1
Carbon dioxide	6.	8.	12.
Four hours			
Manganese	9.5	10.0	0.0
Iron	0.8	0.1	0.0
Alkalinity	358.	358.	342.
Dissolved oxygen	5.6	4.0	4.0
Six hours			
Manganese	10.0	10.0	0.0
Iron	0.8	0.0	0.0
Alkalinity	356.	354.	340.
Dissolved oxygen	5.7	4.5	3.5

sand has removed all the iron, but has not reduced the manganese to an extent which could be detected analytically. The dissolved oxygen content in all cases shows a reduction of over 1 part per million by passage thru the filters, even the one in which no manganese removal is apparently taking place. Filtration thru the filter containing sand and manganese dioxide has removed all manganese and iron, reduced the alkalinity 14 parts per million, and reduced the dissolved oxygen to about the same extent to which it was reduced in the sand filter.

In order to determine the effect of adding a coagulant, two grains per gallon of alum were added after the artificial water had been prepared. The water was aerated, and allowed to settle one hour as before. The results of the operation of the filters under these conditions are shown in Table XXVIII.

The results obtained indicate little change due to the addition of the coagulant. Complete removal of manganese was obtained in the filter containing sand coated with manganese dioxide, and practically no removal in the filter containing sand alone.

The action when iron and manganese were both present was studied by using a mixture of distilled water and tap water in which 10 parts per million of manganese as $MnSO_4 \cdot 4H_2O$ and 10 parts per million of iron as $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ had been dissolved. After this

TABLE XVIII.

MANGANESE REMOVAL BY AERATION AND FILTRATION

2 grains per gallon of alum added. Alkalinity before treatment 356.

(Results are stated in parts per million)

At Start	Unfiltered	Filtered thru	
		Sand	Sand coated with MnO_2
Manganese	5.0	4.8	0.0
Iron	0.2	0.0	0.0
Alkalinity	340.	340.	328.
Dissolved oxygen	8.0	6.5	6.5
Two hours			
Manganese	5.0	4.7	0.0
Iron	0.2	0.0	0.0
Alkalinity	338.	338.	330.
Dissolved oxygen	8.0	7.2	6.0
Four hours			
Manganese	5.0	4.8	0.0
Iron	0.2	0.05	0.0
Alkalinity	340.	338.	328.
Dissolved Oxygen	8.0	7.0	6.2
Six hours			
Manganese	4.8	5.0	0.0
Iron	0.2	0.2	0.0
Alkalinity	336.	334.	330.
Dissolved oxygen	7.5	7.0	6.0

water had been aerated, it had a high, reddish brown turbidity caused by precipitated ferric hydroxide. The results of the treatment are shown in Table XXIX.

Again we have complete removal of iron but no removal of manganese in the sand filter. In the other filter, however, both manganese and iron have been completely removed. In this experiment the alkalinity seems not to have been lowered by passing thru either filter. This is not in accordance with the theory, as the removal should have reduced the alkalinity by an amount equivalent to the manganese removal. This condition might be accounted for either by the presence of small amounts of substances capable of neutralizing free acid in the sand, or by an oxidation of the manganous salt to a marked degree in the aeration and yet to a degree not sufficient to form an insoluble compound.

While no removal of manganese by the sand filter could be detected by analysis, it was found that the upper part of the sand became discolored by a very faint deposit of manganese dioxide after the filter had been in use for some time. This shows that there must have been at all times some slight removal by aeration and filtration. It can readily be seen how this slight deposit would very rapidly aid in the removal of more manganese and increase in amount, until after a time, a deposit of manganese dioxide would have formed in large amounts. This,

TABLE XXIX.

MANGANESE REMOVAL BY AERATION AND FILTRATION

(Results are stated in parts per million)

At Start	Unfiltered	Filtered thru	
		Sand	Sand coated with MnO_2
Manganese	10.0	10.0	0.0
Iron	5.0	0.1	0.0
Alkalinity	24.	26.	30.
Dissolved oxygen	7.3	7.4	2.9
Two hours			
Manganese	9.5	10.0	0.0
Iron	4.8	0.0	0.0
Alkalinity	24.	24.	30.
Dissolved oxygen	7.6	7.5	2.8
Four hours			
Manganese	9.0	10.0	0.0
Iron	5.0	0.0	0.0
Alkalinity	22.	24.	30.
Dissolved oxygen	7.6	7.8	6.0
Six hours			
Manganese	10.0	9.0	0.0
Iron	4.8	0.0	0.0
Alkalinity	24.	24.	28.
Dissolved oxygen	7.6	7.8	7.0

when large enough, would completely remove the manganese from water filtered thru it, and the process might be erroneously considered to be simply one of aeration and sand filtration when in reality it is a catalysis by manganese dioxide.

MANGANESE REMOVAL PLANTS IN ILLINOIS

There are two plants in Illinois, where manganese is efficiently removed from surface water supplies by this method of filtration thru sand coated with a layer of manganese dioxide. One of these filter plants was installed for the purpose of manganese removal, as well as for hygienic purification of a water supply. The other was constructed for the latter purpose only, the presence of manganese in the water not being suspected. For some time after the installation of these plants there was evidence of unsatisfactory manganese removal, but after a period had elapsed for the deposition of a sufficient amount of manganese dioxide in the filters, very efficient removal of manganese resulted.

As no similar observations have been reported by other workers, a description of these two plants with some of the operating results are presented.

MANGANESE REMOVAL AT ANNA, ILLINOIS.

The water works of the Anna State Hospital, in southern Illinois, are located about two miles from the city of Anna, and is about three and one half miles from the hospital buildings. The plant was put in operation in January, 1914.

There are two sources of supply somewhat similar in character. About one half of the supply is from an impounding reservoir, on Kohler creek, having a storage capacity of two million gallons. This reservoir is fed by springs which bubble up over the bottom, as well as by rainfall on the water shed. The other half of the water used is taken from Wilson creek, a nearby stream.

The following analyses made in October, 1914, may be taken as representative of the mineral content of these two sources of supply.

MINERAL CONTENT OF THE WATER SUPPLY OF THE ANNA STATE HOSPITAL

(Amounts are stated in parts per million)

I O N S		Wilson creek supply	Reservoir supply
Potassium	K	5.6	4.7
Sodium	Na	17.8	11.8
Magnesium	Mg	12.6	7.5
Calcium	Ca	78.6	43.9
Iron	Fe	1.0	0.6
Manganese	Mn	trace	1.4
Alumina	Al_2O_3	1.2	3.0
Silica	SiO_2	18.2	6.3
Nitrate	NO_3	5.3	4.0
Chlorine	Cl	3.0	1.0
Sulfate	SO_4	5.2	11.1

HYPOTHETICAL COMBINATIONS

Potassium Nitrate	KNO_3	8.6	6.5
Potassium Chloride	KCl	6.3	2.1
Potassium Sulfate	K_2SO_4	---	2.4
Sodium Sulfate	Na_2SO_4	7.7	14.5
Sodium Carbonate	Na_2CO_3	35.2	10.8
Magnesium Carbonate	$MgCO_3$	43.6	26.0
Calcium Carbonate	$CaCO_3$	196.2	109.8
Iron Carbonate	$FeCO_3$	2.0	1.2
Manganese Carbonate	$MnCO_3$	trace	2.9
Alumina	Al_2O_3	1.2	3.0
Silica	SiO_2	18.2	6.3
Bases	---	2.0	0.0
	Total	321.0	185.5

It will be noted that the Wilson creek supply contains practically no manganese, but that the reservoir supply contains a large amount.

The manganese content of the reservoir supply varies widely at different times, as later data will show. The water has a low turbidity, color and bacterial content for surface waters in Illinois. It contains a large amount of dissolved oxygen, and very little carbon dioxide. Determinations showed 9.8 parts per million of dissolved oxygen, and 3 parts per million of carbon dioxide when the temperature of the water was 20°C.

The water is treated by the ordinary process of mechanical filtration. About 1 grain per gallon of alum is added after which the water passes thru a sedimentation basin having a retention period of four hours. At the outlet of the sedimentation basin calcium hypochlorite is added at the rate of 0.2 parts per million of available chlorine, after which the water passes to the filters. There are three concrete filter units each having a capacity of 300,000 gallons per twenty-four hours. The nominal rate of filtration is 125,000,000 gallons per acre per day. The filters contain 9 inches of gravel and 30 inches of sand. The latter, when put in use, had an effective size of 0.55 mm. and a uniformity coefficient of 1.43.

The presence of manganese in a surface water of

this character containing so much dissolved oxygen was not suspected until complaint was received from the local authorities that the filtered water was causing serious stains on white plumbing fixtures. Great trouble was also experienced when it was used in the laundry, as all fabrics were stained a pale yellow. The first test for manganese was made on July 22, 1914, and a content of 12 parts per million was found in the raw water. This is of course very high. Subsequent tests were made on the untreated and treated water on July 30, and on October 5, 1914. The results obtained are shown below.

Date	Impounding reservoir	Wilson creek	Filter effluent
July 22, 1914	12.0	---	---
" 30, "	7.5	.05	.05
Oct. 5, "	1.4	trace	.0

The manganese content of the water from the reservoir had dropped on July 30th to 7.5 parts per million or about half the amount found on July 22nd. On October 30th, the amount found was only 1.4 parts per million. Analyses of the raw water and the filtered water show an efficient removal of manganese by the treatment which the water received.

In order to determine the cause of this removal, a visit to the plant was made in December, 1914, and arrangements were made to have manganese determinations made as a routine procedure in the laboratory of the water works.

Almost exactly one half of the supply is obtained from the storage reservoir. The other half is from Wilson creek, which furnishes a water containing practically no manganese. It was impossible to obtain representative samples of the raw water directly, as both the reservoir and the creek supplies enter the settling basin thru separate inlets, and thoroly mixed samples of raw water cannot be obtained until they emerge. From December 1 to February 11, determinations of manganese in the water from the reservoir were made, and one half of this value was taken as the true manganese content of the raw water used. From February 11 to May 4, however, actual determinations were made in the water at the outlet of the settling basin . It was found by actual determination that the manganese content in the water at this point was about half that of the water from the reservoir, showing that the amounts as calculated were sufficiently accurate.

The determinations were made by the persulfate method using 50 cc. samples. Only figures in the first decimal place are, therefore, significant. The results obtained in tests made from December 1 to May 4 are shown in Table XXX.

Manganese could be detected in the filtered water in only seven of the one hundred tests made. In the other ninety-three it was absent. The water applied to the filters during this period had a manganese content of

TABLE LXX..

MANGANESE REMOVAL AT ANNA, ILLINOIS

(Amounts are stated in parts per million)

Date 1914	Reservoir	Raw water	Filtered water
Dec. 1	1.5	0.7	0.2
" 2	2.0	1.0	0.2
" 3	1.0	0.5	0.0
" 5	1.2	0.6	0.1
" 7	1.4	0.7	0.0
" 9	0.8	0.4	0.0
" 11	1.2	0.6	0.0
" 13	1.4	0.7	0.0
" 15	1.2	0.6	0.0
" 17	1.8	0.9	0.0
" 19	1.9	1.0	0.0
" 21	1.7	0.8	0.0
" 23	1.1	0.6	0.0
" 29	2.0	1.0	0.0
" 31	1.7	0.9	0.0
1915			
Jan. 1	1.6	0.8	0.0
" 3	1.8	0.9	0.0
" 5	2.1	1.0	0.0
" 7	2.2	1.1	0.0
" 9	2.1	1.1	0.0
" 11	2.1	1.1	0.0
" 13	1.9	0.9	0.0
" 15	1.8	0.9	0.0
" 17	1.7	0.9	0.0
" 19	1.6	0.8	0.0
" 21	1.6	0.8	0.0
" 23	1.4	0.7	0.0
" 25	1.4	0.7	0.0
" 27	1.6	0.8	0.0
" 29	1.8	0.9	0.0
" 31	1.9	1.0	0.0
Mar. 27	0.2	0.0	0.0
" 29	0.2	0.1	0.0
" 30	0.3	0.2	0.0
" 31	0.3	0.0	0.0

Date 1915	Reservoir	Raw water	Filtered water
Feb. 1	1.6	0.8	0.0
" 3	1.4	0.7	0.0
" 5	1.2	0.6	0.0
" 7	1.6	0.8	0.0
" 9	0.8	0.4	0.0
" 11	0.5	0.3	0.0
" 13	0.4	0.2	0.0
" 15	0.2	0.1	0.0
" 17*	0.0	0.0	0.0
" 19*	0.0	0.0	0.0
" 21	0.2	0.1	0.0
" 23	0.2	0.0	0.0
" 25	0.2	0.1	0.0
" 27	0.3	0.1	0.0
Mar. 1	0.4	0.2	0.0
" 2	0.4	0.1	0.0
" 3	0.5	0.2	0.0
" 4	0.6	0.4	0.2
" 5	0.4	0.2	0.0
" 6	0.4	0.2	0.1
" 8	0.6	0.4	0.1
" 9	0.4	0.2	0.0
" 10	0.2	0.0	0.0
" 11	0.2	0.0	0.0
" 12	0.2	0.0	0.0
" 15	0.4	0.2	0.1
" 16	0.4	0.1	0.0
" 17	0.6	0.2	0.0
" 18	0.4	0.2	0.0
" 19	0.4	0.1	0.0
" 20	0.5	0.3	0.0
" 22	0.4	0.2	0.0
" 23	0.2	0.1	0.0
" 24	0.2	0.1	0.0
" 25	0.2	0.0	0.0
" 26	0.4	0.2	0.0

*Heavy rains.

TABLE XXX.. (Concluded)

Date 1915	Reser-voir	Raw water	Filtered water
Apr. 1	0.2	0.1	0.0
" 2	0.2	0.0	0.0
" 3	0.1	0.0	0.0
" 5	0.2	0.2	0.0
" 6	0.3	0.1	0.0
" 7	0.3	0.0	0.0
" 8	0.3	0.1	0.0
" 9	0.4	0.2	0.0
" 10	0.4	0.2	0.0
" 12	0.4	0.1	0.0
" 13	0.3	0.1	0.0
" 14	0.3	0.1	0.0
" 15	0.4	0.2	0.0
" 16	0.3	0.0	0.0
" 17	0.5	0.3	0.0
" 19	0.4	0.0	0.0
" 20	0.5	0.3	0.0
" 21	0.4	0.2	0.0
" 22	0.3	0.1	0.0
" 23	0.4	0.2	0.0
" 24	0.5	0.3	0.0
" 26	0.3	0.2	0.0
" 27	0.4	0.3	0.0
" 28	0.4	0.2	0.0
" 29	0.5	0.3	0.0
" 30	0.3	0.1	0.0
May 1	0.3	0.1	0.0
" 3	0.6	0.4	0.0
" 4	1.0	0.5	0.0

from .0 to 1.0 part per million. The removal is, therefore, very efficient.

The manganese content of the reservoir supply has been slowly decreasing since the summer of 1914. In March and April, 1915, the content was from .2 to .6 part per million, while in December, 1914, it was from 1.0 to 2.0 parts per million.

In order to determine what effect, if any, treatment with hypochlorite had upon the removal, the application of this chemical was omitted during the period from May 1 to May 4. An effluent free from manganese was obtained during this period as before, showing that as good results were obtained without as with bleach.

The walls of the concrete filter units at Anna were covered with a layer of manganese dioxide which in appearance resembled asphalt paint.

Samples of the filter sand were collected for examination. The sand was black in appearance, altho the incrustation was not sufficient to increase the size of the grains greatly. The incrustation was somewhat tenacious, but when the sand was stirred with water in a beaker, some of the deposit became detached.

The sand was analyzed with the following results:

	Percentage
Insoluble in HCl	98.25
Soluble in HCl	1.75
Loss on ignition	0.91
The soluble portion consists of:	
Ferric oxide, Fe_2O_3	16.8
Alumina, Al_2O_3	26.5
Manganese dioxide, MnO_2	12.0
Loss on ignition	54.

Microscopic examination of the sediment washed from the sand grains as well as of the sediment from the water used in washing the filters showed the presence of diatoms and algae, but no organisms resembling Crenothrix were found. The material consisted chiefly of debris, such as sand, clay, and precipitated hydroxides of manganese, iron, and aluminium.

The presence of manganese dioxide in the incrustation on the filter sand is sufficient to account for the removal of the manganese. Some experiments were undertaken, however, to determine whether or not manganese dioxide was the only factor in the process.

The two experimental filters, one containing sand and the other sand impregnated with manganese dioxide which had been used in the former experimental work with artificially prepared waters, were taken to Anna, and used for filtering the raw water. The raw water contained 9.6 parts per million of dissolved oxygen and 3 parts per million of free carbon dioxide. Its temperature was 20°C. The re-

sults obtained are shown in Table XXXI. Complete removal of manganese was obtained when the filter containing manganese dioxide was used. Only a very slight removal of manganese was obtained when the filter containing sand alone was used. This filter, however, had been used for similar work previously, and a small amount of manganese dioxide may very probably have been present on the sand grains, when the experiments were made, thus aiding the removal.

In order to test the theory more completely, the raw water was filtered thru another pair of filters. One of these contained some of the unused sand with which the large filters at Anna are equipped, and the other contained sand which was taken from the filters, after having been used for nearly one year. This latter sand was coal black in color, due to the coating of manganese dioxide which had formed on the grains. The results of these experiments are shown in Table XXXII. Complete removal of manganese was obtained with the used sand, and practically no removal was obtained with the unused sand.

The city of Dresden, Germany, has installed a manganese removal plant which is described by Vollmar.*

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*J. Gasbel. 57, 944-8, 956-9. (1914)

In the process, the water is filtered thru a growth of manganese depositing microorganisms by which the manganese

TABLE XXXI.

MANGANESE REMOVAL BY FILTRATION AT ANNA, ILLINOIS, I.

Experimental filters of sand and of sand artificially coated with MnO_2.

(Parts per million of manganese)

Raw	Filtered thru	
	Sand	Sand coated with MnO_2
1.0	0.8	0.0
1.0	1.0	0.1
1.0	0.9	0.0
1.0	0.9	0.0

TABLE XXXII.

MANGANESE REMOVAL BY FILTRATION AT ANNA, ILLINOIS, II.

Experimental filters of unused sand and of sand after use, naturally coated with MnO_2

(Parts per million of manganese)

Raw	Filtered thru	
	Unused sand	Used sand
1.0	1.0	0.0
1.0	1.2	0.0
1.0	1.0	0.0
1.0	1.0	0.0

in the water is removed.

In microscopic examinations of the filter sand and the sediment in the wash water from the plant at Anna, no microorganisms of this character could be detected. In order to test the possibility of their significance in the removal, however, some of the black sand which had been in use for several months, and which was removing the manganese, was sterilized in the autoclave. A filter was then prepared from this sterilized sand, and after washing until free from manganese, a solution of 5 parts per million of manganese as $MnSO_4 \cdot 4H_2O$ in distilled water was filtered thru it. The results obtained are shown in Table XXXIII.

TABLE XXXIII.

MANGANESE REMOVAL BY FILTRATION AT ANNA, ILLINOIS, III.

Experimental filter of sterilized used sand.

(Parts per million of manganese.)

Raw	Filtered thru	
	Unused sand	Used sand sterilized
5.0	4.8	.0
5.0	5.0	.0
5.0	5.0	.0
5.0	5.0	.0

Complete removal of manganese was obtained by filtration thru the sand after it had been sterilized.

This proves conclusively that the deposit of manganese dioxide on the sand grains effects the removal of manganese. The deposit, however, has formed gradually by the very slight deposition of manganese from the manganese bearing water assisted by direct oxidation by the dissolved oxygen. The dissolved oxygen in the raw water which is always present in large amounts evidently oxidizes the lower oxide of manganese which is formed to the dioxide, at the same time the manganese is removed. The process is therefore catalytic and no regeneration is necessary. When the filter is washed, the grains of sand are stirred up, and the friction very probably is sufficient to keep the manganese dioxide coating scoured off to a degree sufficient to prevent difficulty in the operation of the plant.

MANGANESE REMOVAL AT MOUNT VERNON, ILLINOIS

Mt. Vernon, a city of approximately 8,000 population, is located in the central part of Jefferson County, Illinois. The water supply is obtained from two sources. The principal source of supply is an impounding reservoir fed chiefly by springs which bubble up in the bottom. Casey Fork, a branch of the Big Muddy river furnishes an auxiliary source of supply. An impounding reservoir has been constructed on Casey Fork and from this, water is

pumped into the other reservoir which is fed by springs.

The character of these two supplies is shown by the following analyses of the mineral content.

MINERAL CONTENT OF THE WATER SUPPLY OF MOUNT VERNON, ILLINOIS.

(Amounts are stated in parts per million)

I O N S		Casey Fork	Reservoir
Potassium	K	7.6	8.3
Sodium	Na	9.3	13.1
Magnesium	Mg	10.0	17.6
Calcium	Ca	13.2	23.3
Iron	Fe	0.1	1.6
Manganese	Mn	trace	1.15
Alumina	Al_2O_3	2.0	1.0
Silica	SiO_2	17.4	7.0
Nitrate	NO_3	6.0	2.7
Chlorine	Cl	3.0	5.0
Sulfate	SO_4	62.1	130.8
Bases	---	5.4	3.8
HYPOTHETICAL COMBINATIONS			
Potassium Nitrate	KNO_3	9.8	4.4
Potassium Chloride	KCl	6.3	10.5
Potassium Sulfate	K_2SO_4	0.9	2.2
Sodium Sulfate	Na_2SO_4	28.7	40.0
Magnesium Sulfate	$MgSO_4$	49.4	87.0
Calcium Sulfate	$CaSO_4$	3.5	45.8
Calcium Carbonate	$CaCO_3$	30.5	24.5
Iron Carbonate	$FeCO_3$	0.2	3.3
Manganese Carbonate	$MnCO_3$	trace	2.3
Alumina	Al_2O_3	2.0	1.0
Silica	SiO_2	17.4	7.0
Bases	---	5.4	3.8
	Total	154.1	231.8

Both supplies have a high percentage saturation of dissolved oxygen.

The water is treated with alum at the rate of about one half a grain per gallon. After sedimentation it is treated with calcium hypochlorite at the rate of .2 to .3 parts per million of available chlorine. There are three concrete filters, each having a capacity of 500,000 gallons per day, operating at a rate of 125,000,000 gallons per acre per day.

The results of the manganese determinations made in the raw and in the filtered water from January, 1914, to April, 1915, are shown in Table XXXIV. The determinations since December 1, 1914, were made in the water works laboratory at Mt. Vernon.

It will be noted that there is a rather wide variation in the manganese content of the untreated water. The range is from .05 to .8 parts per million over a period of one year. The efficiency of the plant for the removal of manganese is well shown by a comparison of the results for the raw and the filtered water.

The manganese content of the filtered water has ranged from .0 to .2 parts per million. On 35 of the 65 days on which tests were made no manganese was found in the filtered water.

The filter sand used at this plant was coated with a dark colored substance, which upon analysis was found to contain a large amount of manganese. The results of the

TABLE XXXIV.

MANGANESE REMOVAL AT MOUNT VERNON, ILLINOIS

(Parts per million of manganese)

Date 1914	Raw water	Filtered water	Date 1915	Raw water	Filtered water
Jan. 9	0.4	0.2	Feb. 16	0.4	0.0
Feb.16	0.4	0.25	" 18	0.5	0.1
Mch.24	0.5	0.1	" 20	0.4	0.0
July23	0.05	0.05	" 23	0.5	0.0
Aug.18	0.12	0.12	" 25	0.5	0.0
Oct.14	0.4	0.0	" 28	0.4	0.0
Dec. 2	0.4	0.0			
" 5	0.4	0.0	Mch. 2	0.4	0.1
" 7	0.4	0.0	" 4	0.4	0.1
" 9	0.4	0.0	" 6	0.4	0.1
" 11	0.4	0.0	" 15	0.4	0.0
" 14	0.6	0.2	" 18	0.4	0.1
" 16	0.6	0.2	" 20	0.3	0.0
" 19	0.7	0.1	" 23	0.3	0.0
" 21	0.7	0.2	" 25	0.3	0.0
" 23	0.8	0.1	" 27	0.3	0.0
" 26	0.6	0.0	" 29	0.3	0.0
" 28	0.6	0.1	" 31	0.2	0.0
" 31	0.6	0.1			
1915					
Jan. 4	0.6	0.1	Apr. 2	0.3	0.1
" 6	0.6	0.1	" 5	0.2	0.0
" 9	0.6	0.0	" 6	0.2	0.0
" 12	0.7	0.1	" 8	0.2	0.0
" 13	0.7	0.2	" 10	0.2	0.0
" 15	0.8	0.2	" 12	0.2	0.0
" 18	0.8	0.3	" 13	0.2	0.0
" 22	0.8	0.3	" 16	0.2	0.0
" 23	0.8	0.2	" 17	0.2	0.0
" 25	0.7	0.1	" 22	0.3	0.0
" 27	0.7	0.0	" 24	0.3	0.0
" 29	0.6	0.0			
Feb. 1	0.6	0.1			
" 3	0.6	0.2			
" 6	0.6	0.1			
" 9	0.4	0.0			
" 12	0.4	0.0			
" 15	0.4	0.0			

analysis of the sand are shown below.

	Percentage
Insoluble in HCl	99.01
Soluble in HCl	.99
Loss on ignition	.43

The soluble portion is:

Ferric oxide,	Fe_2O_3	4.8
Alumina,	Al_2O_3	27.7
Manganese dioxide,	MnO_2	35.0
Loss on ignition		43.

When examined microscopically before washing, no Crenothrix or similar organisms were found. The wash water contained, clay, dirt, inert matter, diatoms, chlorophyl bearing algae, debris, etc.

The filter medium used at this plant is, therefore, very similar to that used at the Anna plant. The incrustation of the sand is not so great, and, therefore, the amount of manganese dioxide present is somewhat smaller. This fact probalby explains the somewhat lower efficiency of removal at Mt. Vernon compared with that obtained at Anna. The removal is effected, however, in exactly the same way as at Anna, namely, by filtration thru sand coated with a layer of manganese dioxide, the latter effecting the removal.

INCRUSTATION OF WATER PIPES BY MANGANESE BEARING WATERS

The fact that the use of a water which carries only a small amount of manganese will cause serious incrustation of water pipes, has been noted by many workers. The incrus-

tations consist chiefly of oxides of manganese and iron.

R. S. Weston* gives the analyses of three such

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*Trans. Am. Soc. C. E., 64, 112-204. (1909)
Jour. N.E. Water Works Assn. 28, 31. (1914)

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incrustations, collected from the water mains at Hannover in Germany, and analyzed by him. The largest amount of manganese present was 7.15 percent.

E. V. Raumer* found an incrustation in the water

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*Z. anal. Chem. 42, 590-602. (1902)

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supply of Fürth which contained 43.85 percent. Mn_3O_4. The original water contained 2 parts per million of Mn. Threadlike organisms resembling Crenothrix were found.

of the clogging of pipes by manganese waters are presented by E. H. S. Bailey,[1] D. D. Jackson,[2] Beythien, Hempel and Kraft,[3] Volmar,[4] and others.

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1. J. Am. Chem. Soc., 26, 714. (1904)
2. J. Soc. Chem. Ind., 21, 681. (1902)
3. Z. Nahr. Genussm. 7, 215. (1904)
4. J. Gasbel. 57, 944. (1914)

Most of these investigators attribute the action to the growth of iron and manganese bacteria which deposit the oxides of these metals in their sheaths.

Similar incrustations have caused serious difficulty in the water supplies of Mt. Vernon and Peoria, Illinois. The composition of these deposits is reported by Bartow and Corson.*

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*University of Illinois Bulletin,
State Water Survey Series No. 10, 64. (1913)

In a microscopic examination of these deposits, no organisms resembling Crenothrix could be found. Specimens from the water supplies of Mt. Vernon, Peoria, Anna, and Springfield, were found to contain large amounts of iron and manganese, but none of the oxide depositing bacteria. These incrustations, moreover, did not present the threadlike, filamentous appearance which is usually characteristic of Crenothrix growths.

In view of the importance of the catalytic effect of manganese dioxide in removal processes, it seems very probable that this substance is responsible for the formation of the incrustations where organisms do not play a part. If a manganese bearing water containing dissolved oxygen is pumped into a distribution system, there is undoubtedly a very slight precipitation of manganese as the hydrated dioxide. This dioxide now reacts with the manganous salt in the water removing it by chemical reaction to form a lower oxide. The dissolved oxygen present, however, simultaneously oxidizes this lower oxide to manganese dioxide. The process is,

therefore, catalytic, and is exactly the same as in the removal of manganese in a manganese dioxide filter.

Since acid is formed as one of the products of reaction when manganese is removed, the hydrogen ion concentration of the water determines the point at which equilibrium is reached. Free carbon dioxide in solution renders water acid. Sodium, calcium and magnesium bicarbonates, on the other hand, render water alkaline because they are hydrolyzed. Both carbon dioxide and bicarbonates are usually present, and the question of whether a water is acid or alkaline depends on the relative amounts of each. It is clear that the lower the free carbon dioxide content and the higher the bicarbonate content, the lower will be the hydrogen ion concentration, and, therefore, the greater the tendency for the precipitation of manganese.

CONCLUSIONS

The principle underlying all processes for the removal of manganese from water supplies, except those of direct chemical precipitation, is the reaction between manganous salts and manganese dioxide to form a lower oxide.

The removal of manganese by the Permutit process takes place according to this reaction, since the state of oxidation of manganese in the substance is not greater than in manganese dioxide. This is agreement with the view of Tillmans. We find no evidence of the existence of oxides

higher than MnO_2 in this substance, contrary to the suggestion of Gans and the Permutit Company.

On an experimental scale, no appreciable manganese removal was obtained by aeration and sand filtration as reported by Thiesing, Weston and Barbour. When an artificial coating of manganese dioxide was prepared on the sand grains, however, complete removal of manganese was obtained. Manganese is efficiently removed from water supplies at Anna,.and at Mt. Vernon, Illinois, by this process a coating of manganese dioxide having formed on the sand. If the water contains dissolved oxygen, regeneration of the filter is unnecessary, and the process may be considered as catalytic.

The success of the aeration and sand filtration process as used by Thiesing, Weston and Barbour is in reality due to the action of manganese dioxide, and not to aeration and sand filtration alone. The assumption that manganese may be removed by the same process which removes iron is incorrect.

The formation of manganese incrustations in water pipes, in those cases where manganese bacteria are not concerned, is explained by the catalytic action of manganese dioxide.

BIOGRAPHICAL

The writer received his early education in the public schools of Concord and Laconia, New Hampshire. He was graduated with the degree of Bachelor of Science from New Hampshire College in 1910. In 1913, he received the degree of Master of Science from the University of Illinois.

From 1910 to 1911 he was assistant in Chemistry, and from 1911 to 1915, Assistant in Sanitary Chemistry in the University of Illinois. From 1911 to 1912 he was chemist in the State Water Survey, and from 1912 to 1915, chemist and bacteriologist in the same department.

His publications are:

With Charles L. Parsons,

The Solubility of Barium Nitrate and Barium Hydroxide in the Presence of Each Other.

J. Am. Chem. Soc., 1383-7. (1910)

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Proc. Ill. Water Supply Assn., 114-29. (1911)

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The Occurrence of Manganese in the Water Supply and in an Incrustation in the Water Mains at Mt. Vernon, Illinois.

Univ. of Ill. Bull., State Water Survey Series No. 10, 56-65. (1913)